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COMMUNICATIONS
FROM THE
PHYSICAL LABORATORY
AT
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COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

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p. 6 line 3 from the top: for IX read XII.

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(*Versl. Kon. Akad.* **September** 1912).

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(*Versl. Kon. Akad.* **October** 1912).

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(*Versl. Kon. Akad.* **November** 1912).

132*c*. **Bengt Beckman.** On the Hall effect, and on the change in resistance in a magnetic field at low temperatures VII. The Hall effect for gold-silver alloys at temperatures down to the melting point of hydrogen
(*Versl. Kon. Akad.* **December** 1912).

132*d*. **H Kamerlingh Onnes** and **Bengt Beckman.** On the Hall effect, and on the change in electrical resistance in a magnetic field at low temperatures. VIII. The Hall effect in Tellurium and Bismuth at low temperatures down to the melting point of hydrogen.
(*Versl. Kon. Akad.* **December** 1912).

132*e*. **H. Kamerlingh Onnes** and **E. Oosterhuis**. Magnetic Researches. VII. On paramagnetism at low temperatures (continued).
(*Versl. Kon. Akad.* **Januari** 1913).

132*f*. **H. Kamerlingh Onnes** and Mrs. **Anna Beckman.** On piezo-electric and pyro-electric properties of quartz at low temperatures down to that of liquid hydrogen.
(*Versl. Kon. Akad.* **Februari** 1913).

132*g*. **Bengt Beckman.** Measurements on resistance of pyrite at low temperatures, down to the melting point hydrogen.
(*Versl. Kon. Akad.* **Februari** 1913).

To be inserted in the above index.

121*c*. **H Kamerlingh Onnes** and **C. A. Crommelin.** Isotherms of monatomic substances and of their binary mixtures XI. Remarks upon the critical temperature of neon and upon the melting point of oxygen.
(*Versl. Kon. Akad.* **Mei** 1911).

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(*Cong. Intern. du froid, Paris.* **Octobre** 1908).

21*b*. **H. Kamerlingh Onnes.** Bericht über im Cryogenen Laboratorium zu Leyden ausgeführte Untersuchungen
(*Intern. Kältekongress, Wien.* **October** 1910).

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(*Versl. Kon. Akad.* **October** 1911).

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(*Chemisch Weekblad* **Februari** 1911).

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(*Versl. Kon. Akad.* **April** 1912).

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(*Versl. Kon. Akad.* **April** 1912).

25. **W. H. Keesom.** On the second virial coefficient for diatomic gases.
(*Versl. Kon. Akad.* **September** 1912).

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(*Versl. Kon. Akad.* **October** 1912).

27. **Albert Perrier et H. Kamerlingh Onnes.** La susceptibilité initiale du nickel aux très basses températures.
(*Archives des sciences phys. et natur.* 4^{ième} *période*, *tome* 34. **Decembre** 1912).

Suppl. N⁰. 23 has been published as a separate volume.

For insertion in Volume XII, No. **121—132.**

Erratum Communication No. 121a.

Title-page and p. 3: in the title read “IX” for “VIII”.

Erratum Communication No. 121b.

p. 21, line 11 from the bottom: for “1019” read “10”.

Errata Communication No. 122a.

p. 4, line 1 from the bottom: for “occured” read “occurred”.
„ 5, „ 11 „ „ top: after “it” insert “is”.

Errata Communication No. 124b.

Title-page and p. 11: in the title read “XII” for “IX”.
p. 16, line 6 from the top: for “hower” read “however”.

Addendum Communication No. 124c.

p 23, line 4 from the bottom: after “the” insert “wire of”.

Erratum Communication No. 125.

p. 4, line 21 from the bottom: for “hem” read “them”.

Erratum Communication No. 126.

Title-page: in the title read “initial” for “inital”.

Erratum Communication No. 127.

p. 28, line 4 from the bottom: for “981.625” read “980.625”.

Errata Communication No. 128.

p. 4, line 16 from the bottom: for “B^A” read “B_A”.
„ 8, „ 2 „ „ top: for “an” read “and”, for “das” read “as”.

Erratum Supplement No. 21b.

p. 45, line 12 from the bottom: for “Ereignisse” read “Ergebnisse”.

Erratum Supplement No. 22a.

p. 6. in the denominator of the last fraction of the equation:

for “$\dfrac{\partial_2 \psi}{\partial x \, \partial x}$” read “$\dfrac{\partial^2 \psi}{\partial x \, \partial v}$”.

Erratum Supplement No. 22b.

p. 15, line 10 from the top: for “5” read “13”.

Errata Supplement No. 24.

p. 37, in formula (47): for “$\dfrac{3}{4}\pi\tau^3$” read “$\dfrac{4}{3}\pi\tau^3$”.

„ „ (48): „ “n_{1b1}” „ “$\dfrac{n_{1b1}}{2}$”.

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21 JUN 1913

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 121a.

W. J. DE HAAS. "Isotherms of diatomic substances and of their binary mixtures. VIII. Control measurements with the volumenometer" (*with three plates*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, **28 April 1911**, p. 1168—1179).

EDUARD IJDO — PRINTER — LEIDEN.

W. J. DE HAAS. "*Isotherms of diatomic substances and of their binary mixtures.* VIII. *Control measurements with the volumenometer.*"

§ 1. *Introduction.* Prof. KAMERLINGH ONNES, with a view to the determination of the compressibility of hydrogen vapour, invited me to make a special study of the volumenometer (see Comm. No. 84) with which these measurements were to be made; the results of this particular investigation are given in the present paper, and, at the same time I have described the improvements mentioned in Comm. No. 117 which were specially introduced for the measurement of the compressibility of hydrogen vapour, and to which reference was then made as to be described later in another paper dealing with that investigation.

The measurements intended necessitated great accuracy in determinations with the volumenometer. While in the researches described in Comm. No. 117 the volume of the gases which were admitted from the dilatometer to the volumenometer could be measured under pretty high pressures ($1 - {}^1/_2$ atm.), and consequently those pressures had to be known with certainty only to 0.05 mm, it is desirable in a determination of the compressibility of hydrogen at very low temperatures (—259 to —252° C.), to measure pressures which may be as low as 10 cm. to one five-thousandth of their value, so that in this case an accuracy of 0.02 mm. is essential. The lowness of the pressures to be measured necessitates a very high degree of accuracy in the pressure measurements. My object in the present investigation was to see in what way these high demands could be satisfied [1]), and to make sure that such was actually the case in the results obtained.

---

[1]) A discussion of the degree of accuracy which was then reached was given by KEESOM in Comm. No. 88 (1903).

§ 2. *Constants.* I. *Determinations of the Volumes.*

As has already been mentioned in Comm. No. 117 § 3, the accurate volumenometer in use in the cryogenic laboratory [1]) described in Comm. No. 84 was re-calibrated, from which at the same time comparisons might be made with the data of Comms. No. 88 and No. 92 and an idea of the acuracy to be reached could be obtained. For this purpose a capillary tap with a fine drawn out nozzle was fused to the lower end of the air-trap at Eb_0 (Pl. I. Comm. No. 84). The calibrations were made with mercury with which the apparatus was filled under high vacuum. During the progress of the calibrations the temperature of the volumenometer was kept constant to within $^1/_{40}$ th of a degree by means of the thermostat described in § 5 [2]).

Each of the bulbs Eb_1 (I, II, III, IV and V of fig. 1 Pl. I Comm. No. 117) was calibrated twice, the auxiliary bulb Eb_2 (cf. Pl. I Comm. No. 84) and the connecting neck Eb_8 were each calibrated four times. The following table contains the old and the new calibrations all of which are reduced to 20° C. From the excellent correspondence obtained, it appears that the screen-method is quite reliable for the positions of the screens on the connecting necks have not altered in any way since Comm. No. 84 (1902). At the same time it is evident that the volumenometer is capable of determining volumes accurately to $^1/_{10000}$ as long as the volumes of the mercury menisci are known with sufficient accuracy.

---

[1]) The volumenometer with its auxiliary apparatus is shown on the left hand side of Pl. I Comm. No. 117 to which belongs fig. 1 Pl. I of Comm. No 84, along with the modifying diagram shown on fig 2 Pl I of this Communication. In connection with fig. 2 Pl. I see also § 4 of this paper. For the arrangement of the volumenometer, scale, cathetometer, etc., see Comm. No. 117. For description of the thermostat see § 5 of this Communication.

[2]) Before proceeding to calibrate the apparatus it was thoroughly cleaned both inside and out. In this process the screen Eg_1 (Pl. I, Comm No. 84) was replaced by a new one, and the optical properties of the glass windows in the jacket were investigated before being replaced.

TABLE I.

Volumes between the marks

	Individual measurements.	Mean.	Deviations from mean.	Former (1902) calibration.	Differences between the two calibrations.
Bulb Eb_2 1)	microliters				
1st calib.	25220	25229	1/5000		
2nd ,,	25233				
3rd ,,	25226				
4th ,,	25236				
Bulb I.					
1st calib.	252584	252589	1/50000	252555	1/8000
2nd ,,	252594				
Bulb II.					
1st calib.	253565	253550	1/17000	253572	1/12000
2nd ,,	253537				
Bulb III and IV.					
1st calib.	505640^0	505640^3	1/2000000	505650	1/50000
2nd ,,	505640^6				
Bulb V.					
1st calib.	252854	252845	1/25000	No comparison possible 2).	
2nd ,,	252837				

---

1) This was not calibrated in 1902.

2) Cf. note 2, pag. 4.

§ 3. II. *Determinations of the optical constants.*

1st Owing to the prismatical shape of the windows in the jacket through which the volumenometer was observed, and 2nd to the circumstance that their surfaces were not accurately vertical, an optical correction had to be applied to the height readings in the volumenometer. The latter correction may be regarded as composed of two distinct parts, 1st a correction in consequence of the deviation from 90° of the inclination to the horizon of the long axis of the apparatus in the plane of incidence, and 2nd a correction in consequence of the angle a_i made at any point i by the outer surface with the long axis of the apparatus.

Of these the first was determined every time from the deviations of a plumb line arranged so that when pointing at the corresponding mark it is parallel to the long axis of the apparatus, or from the deviations of a spirit level laid on a plane perpendicular to the long axis. Both this perpendicular plane and the plumb line mark were firmly attached to the apparatus With a sufficiently careful observation with the plumb line an accuracy of 0.01 mm in the height readings can be attained. By reading the spirit level during this operation one can substitute the simpler level reading for the plumb line. When it is not desired to read to more than 0.05 mm. a simple reading with the plumb line is sufficient.

The angles between the front surfaces of the windows at any point i and the long axis of the apparatus are constants of the apparatus, and need to be re-determined only in the event of the windows being removed. The correction resulting from this angle may be evaluated in either of two ways.

1st *Method.* If the long axis of the apparatus is perfectly vertical the correction to be applied to a reading for a perfectly horizontal beam of light is, for small angles of incidence,

$$A\left(\theta - \frac{\theta}{n_{1\cdot 2}}\right)$$

in which A is the length of the path traversed by the light in water from the point on which the telescope is focussed to the front of the windows (in the apparatus used this distance was

8 cm.), θ is the angle [1]) between the normal to the windows and the horizontal plane, and $n_{1 \cdot 2}$ is the refractive index for air-water. The angle θ was measured by means of a combination level. For this purpose was used a level from a cathetometer by the Société Genevoise (1 scale division = 0,′06) placed upon an auxiliary apparatus (Pl. II fig. 1). This arrangement consisted of an arm *R* turned accurately cylindrical and attached perpendicularly to a heavy copper plate *P*. By means of the three adjusting screws *a*, *b* and *c* this plate *R* can so be placed against a glas comparison surface which has been made accurately vertical that the arm *R* indicates a perfectly horizontal position. The square end of the level is then pressed against the windows of the volumenometer jacket and the level is again brought to the horizontal. From the number of turns of the divided screw head of the screw *c* necessary to accomplish this, from the pitch of the screw *c* which has been determined beforehand, and from the known distance of the point of the screw *c* to the line *ab* the angle θ may be calculated. From this the error in the reading follows at once when the angle of refraction of the window is allowed for. (The application of the combination level assumes that the curvature is negligible which will probably always be the case with plate glass for degrees of accuracy up to 0.05 mm.).

The results are given in Table III, column I (p. 14).

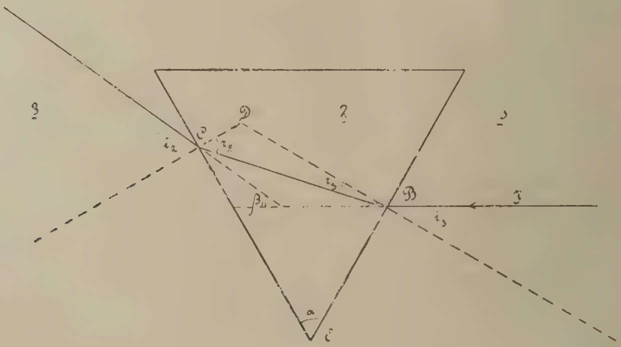
In our present experiments the auxiliary apparatus employed for the spirit level has not yet allowed us to attain with sufficient certainty an accuracy greater than that corresponding to an error of about 0′.3 (that is to say a correction of 0.01 mm.).

The 2nd *Method* of determining the errors in the readings consists of obtaining readings of the heights of the middle mark on the screens when no water is in the jacket and also when the jacket is full. For simplicity this measurement is reduced to a determination of the change in height of one of the marks and the change in distance of the other mark from this one For during the measurement of the differences in height for one mark a layer of water 8 cm. thick is alternately interposed and removed, and therefore the cathetometer must be moved as a whole so as to allow its being focussed upon the standard metre with which every care is taken to ensure its fixed position and to protect it against any temperature change. Absolute height measurements were rendered very tedious on account of this repeated moving of the cathetometer, while the determination of the alteration in the distances between two central lines was comparatively simple. The determinations of the changes in the distances of each line from the fundamental one were, in order to ensure the invariability of the lengths measured, reduced in every case to the determination of the changes in the distances between two successive central lines.

---

[1]) One can easily see that a difference of 1′ in the horizontal position of the telescope (when the distance between the objective and the focussed mark is ± 45 cm.) can have no effect upon an accuracy of 0.01 mm. nor can the deviation of light caused by the glass of the connecting necks when these are carefully constructed.

In the sequel the glass windows, even when they exhibit some curvature, are regarded as prisms, and it is assumed that each of the portions through which the screens are seen — even in the same piece of glass — has an individual angle of refraction. These angles of refraction α_1, α_2 etc., (projected upon the plane which during the height measurements coincides with the vertical plane through the axis of the telescope) were all measured beforehand.



The foregoing figure (in which the ray is projected upon the vertical plane through the axis of the telescope) shows a window in

Erratum Communication N⁰. 121*a*.

p. 9 line 5 from the top: for to read the.

which the prismatic character is strongly accentuated so as to add to the clearness of the drawing. Let I be the incident ray which traverses the axis of the cathetometer telescope supposed horizontal. The media are represented by the indices 1, 2 and 3 Let β_0 represent to total deviation which the ray undergoes at the mark m_0 owing to refraction at the surfaces 1.2 and 2.3; for the sake of simplicity this total deviation will, in the sequel, be referred to as β as long as there is only a single mark involved.

Since

$$\beta = i_1 + i_2 - \alpha$$

we get

$$\beta = (n_{1\cdot 2} - 1)\,\alpha + r_2\,(n_{3\cdot 2} - n_{1\cdot 2}).$$

When there is no water in the volumenometer jacket it follows that

$$\beta = (n_{12} - 1)\,\alpha.$$

Hence, calling the distance of the front surface of the windows from the screens A, we get for the optical correction to be applied to the reading for a line on the screens

$$A\,r_2\,(n_{3\cdot 2} - n_{1\cdot 2}).$$

This difference was repeatedly determined for one of the central lines, the one chosen being the central line of the middle screen, so as to make the deviation errors for the other lines as small as possible. In these measurements allowance is made for the sinking of the volumenometer as a whole when water is admitted; the distances through which it sank were measured each time by focussing a second telescope of the cathetometer upon a mark on the volumenometer.

Further, let the indices e and f of β_0, β_1, β_2 etc., indicate whether they represent the corresponding angles when the volumenometer jacket is empty or when it is full of water, and just as with β, let us write r_{01}, r_{11}, etc., and r_{02}, r_{12}, etc., for the various values of r_1 and r_2; we then get for the distance measured with the jacket empty f. i.

$$A\,(\beta_{1e} - \beta_{2e}) = A\,n_{1\,2}\,\{(r_{11} - r_{21}) + (r_{12} - r_{22})\} - A\,(\alpha_1 - \alpha_2)$$

and when it is full

$$A\,(\beta_{1f} - \beta_{2f}) = A\,n_{1\cdot 2}\,(r_{11} - r_{21}) + A\,n_{32}\,(r_{12} - r_{22}) - A\,(\alpha_1 - \alpha_2).$$

Taking the measured distances $A(\beta_{1e} - \beta_{2e})$ and $A(\beta_{1f} - \beta_{2f})$ in pairs and subtracting the one from the other we obtain the following equations in which V is the difference thus obtained:

$$r_{02} = \frac{V_{01}}{A} \frac{1}{n_{3.2} - n_{1.2}} + r_{12}$$

$$r_{12} = \frac{V_{12}}{A} \frac{1}{n_{3.2} - n_{1.2}} + r_{22}$$

$$r_{22} = \frac{V_{23}}{A} \frac{1}{n_{3.2} - n_{1.2}} + r_{32}$$

$$r_{32} = \frac{V_{34}}{A} \frac{1}{n_{3.2} - n_{1.2}} + r_{42}.$$

Substituting in these equations the value of r_{32} which is directly measured at m_3 we obtain in succession values for r_{22}, etc., and from these the optical deviations are calculated. For example for m_1 from

$$A(n_{1.2} - 1)\,\alpha_1 + A r_{12}(n_{3.2} - n_{1.2}).$$

The numbers thus obtained are given in Tab. III, col. III (p. 14).

§ 4. *Control measurements.*

Partly to verify the results obtained and partly to control the realization of the temperature equilibrium between the various mercury filled parts of the apparatus control measurements were carried out as indicated in § 3 of Comm. N^0. 117 (June 1910) with the mercury at the same pressure in the two communicating vessels, the manometer and the volumenometer. For this purpose the upper portions of the volumenometer and the manometer were brought into communication with each other and the mercury was then driven up until the meniscus stood in one of the connecting necks of the volumenometer; the clamp l_9 (Pl. I fig. 1. cf Pl. I, Comm. N^0. 117) was then closed so as to avoid the effects of vibrations in the mercury in the bulb Q_1 (cf. Pl. I Comm. N^0. 117) caused by gusts of wind or by vibration of the building. Care was always taken to ensure a good vacuum above the two corresponding mercury levels, so as to prevent troublesome expansions and too slow equilibration between the gas in the volumenometer and the manometer. Since in the case of the uppermost necks mercury columns about 1 metre in height had to be kept in hydrostatical equilibrium the greatest care had to be taken to ensure the temperature equilibrium of the mercury column. For this purpose a water jacket was put around the manometer tube being firmly attached to it by means of two rubber corks. In order to reduce to a minimum the optical corrections necessarily introduced by the use of this jacket the holes in the rubber corks were bored to one side of the centre so that the water jacket was thinnest just at the side through which the readings were made. In order to determine the optical corrections fifteen fine lines were etched on the other side of the manometer tube. The heights of these lines were also read on the cathetometer with the volumenometer jacket both empty and full of water. Each of these measurements was repeated sixteen times. Since both the water layer and the air layer through which readings were made were only 4 mm. thick the cathetometer telescope could be kept immovable and the difference could be determined directly each time with the micrometer eyepiece. Parallax errors were avoided by covering one half of the telescope objective with a plate of glass whose optical thickness was the same as that of the water layer in the volumenometer jacket. When the jacket was full readings were taken through the uncovered half of the objective, and when it was empty readings were made through the covered half. The optical error due to the glass plate was determined independently. In this way the optical errors due to the manometer jacket were easily determined with accuracy to within 0.005 mm. From the results it is evident that the use of such a jacket has much to recommend it, while the optical correction appears to be only about 0.03 mm. a value that may in many cases be regarded as negligible.

The manometer jacket was supplied from underneath with water from the thermostat (see § 5). From above the water flowed out through a connecting tube which was well protected from heat exchange with the surroundings to the lower portion of the volumenometer jacket. Hence variations in the temperature of the jacket water occasion errors which neutralise each other at least in part, a result which one cannot be sure of obtaining when the water supplies are independent or form branches of one circuit.

In the room in which readings are taken it is difficult to keep the temperature gradient below $^1/_2$° per metre; it often assumes greater values and, in consequence, it is easy for the mercury in the bulb and in the rubber tubes to assume a temperature different from that obtaining in the mercury colums within the jackets; on this account the water which flows out from the upper end of the volumenometer jacket is utilised to warm or cool as the case may be the mercury which flows from the mercury bulb to the manometer or to the volumenometer. For this purpose the short rubber tubes are joined to the large glass T-piece. The vertical arm of this T-piece is widened so as to obtain a greater surface for heat exchange, and this vertical arm is surrounded by the two copper tubes shown in Pl. I, fig. 1. The water which is flowing off from the volumenometer is then divided into two circuits which traverse these copper tubes and then leave the apparatus I_1 and I_2. By this arrangement are eliminated all undesirable convection currents and conduction phenomena in the masses of mercury.

In conclusion we may mention that all parts of the apparatus were carefully wrapped up so as to protect them from heat exchange with the outside.

After these precautions had been taken a great number of measurements were made of the heights of the menisci in the communicating vessels. The capillary depressions were obtained from KELVIN's graphical constructions in which a mean capillary constant was assumed. After a proper application of the temperature and capillary corrections the optical corrections were calculated as the remaining difference in height. In Table II are collected the mean data obtained from the various measurements which with the help of the method of communicating vessels have led to one of the determinations of the optical constant for the mark m_0. The means of all the measurements are given in Table III, col. IV.

Since there can be no dubiety about the pressure equilibrium a comparison of the optical corrections thus determined with those obtained by the method of the combination level and with those obtained by the removal of the water from the jacket (Table III, cols. II and III) gives an immediate opportunity of judging the degree of accuracy of the pressure measurements. When everything mentioned in the foregoing has been taken into consideration it appears that the pressure is certain to within 0.02 mm. and, in favourable circumstances,

TABLE II.

Control measurement at mark m_0. (Pl. I. Comm. N°. 117).

Neck mark m_0	level	Cath. meter scale.	Eye-piece head	Men. height			
					Temp. of volum. m	below	16.05^5
					jacket at 1 h. 45 m.	above	16.07
Volumenom. men. top.	10	79.024 cm.	21.25	0.181 mm.	Temp. of manom.	below	16.02
,, ,, base	10	78.843	21.25		jacket at 1 h. 45 m.	above	16.10
Manometer men. top.	10		21.20	0.188			
,, ,, base	10		26.37				
Volumenom. men. top. (mean of 7 readings)	10		21.25				
Manometer men. top. (mean of 7 readings)	10		21.21				
Manometer men. top.	10		21.20	0.182	Temp of volum. m.	below	16.30
,, ,, base	10		26.29		jacket at 2 h 15 m.	above	16.13
Volumenom men. top	10	79.024	21.27	0.184	Temp. of manom.	below	16.13
,, ,, base	10	78.840			jacket at 2 h. 15 m.	above	16.11

		Capillary depr.	
		Volumenom.	Manom.
	$1^h 45^m$	0.14^4 mm.	0.04^5
	$2^h.15^m$	0.14^8	0.04^3
	mean	0.14^6	0.04^4
Correction for capillary depression			−0.10^2
Correction for temperature difference between the comm. vessels			
	$1^h 45^m$	none	
	$2^h.15^m$	0.01^4	
	mean		−0.00^7
Optical correction for manom. jacket (see p. 11).			−0.04^0
Actual height difference observed (4/273 mm.)			−0.01^4
Hence optical corr. for volumenometer			−0.12^1

to within 0.01 mm.; it is therefore possible to measure mercury pressures of 10 cm. with certainty to 1 in 10000.

In conclusion it may be mentioned that the heights of the edges of the menisci were read at the near side. As comparatively little light could be introduced into the interior of the volumenometer jacket, readings at the sides of the volumenometer tube were matters of considerable difficulty, but by making them in front sharp readings could be obtained, for, with suitable illumination from an electric hand lamp the meniscus edge could always be seen as a sharp line at which a number of images came to an end. As the near edge of the meniscus was about 8 mm. nearer the objective of the telescope than the top the same artifice was employed to eliminate parallax errors in this method of reading as was indicated above in the determination of the corrections for the manometer. Glasses were placed in front of the telescope objective and were firmly attached to the telescope tube as is shown in Pl. II fig. 2. The optical shortening of the path of the light rays was about 8 mm. By turning the glasses round their axis and thus causing them to approach or recede from each other the adjustments could be made perfectly free from parallax. The top of the

TABLE III.

Comparison of the different measurements.

Neck	Method I	Method II	Control measurem.
Eb_{82}	-0.13^2 mm.	-0.13^3 mm.	-0.12^1 mm.
Eb_{81}	-0.13^2	-0.13^3	-0.12^2
Eb_7	-0.13^2	-0.13^8	-0.15^3
Eb_6	-0.15^9	-0.14^6	-0.15^5
Eb_4	$+0.03^5$	$+0.05^1$	$+0.04^1$
Eb_3	$+0.03^5$	1)	$+0.05^0$

meniscus was read through the glasses and the edge through the uncovered portion of the objective. Optical errors arising from the glasses used in this apparatus and also from those already mentioned as used for the manometer tube were accurately determined beforehand.

§ 5. *The Thermostat.* The thermostat which was used in these control measurements and also in experiments upon the compressibility of hydrogen at ordinary temperature which have already been done but are not yet published was essentially the same as that described in Comm N^0. 70. For a description of the apparatus reference must be made in the first place to that paper. Certain modifications have been introduced with a view to

1^0. better constancy of the temperature during a great time interval and consequently less necessity for constant supervision ; and

2^0. easier adjustment to the desired temperature.

The water vessels have remained the same. A small cylindrical vessel has been introduced immediately after the large one (see Pl. III). The copper spiral with the xylol regulator of the vessel *B* has been removed and in its place has been put (temporarily) a glass spiral of three turns going from the bottom of the vessel *B* upwards. This spiral is bent upwards from below and ends in the gas regulator. A side tube with ground joints connects the spiral with a large thermometric vessel. A rubber connecting piece allows the system to vibrate without damage. The thermometric vessel and the spiral are filled with chloroform and mercury, the mercury being shown black in the figure. The use of chloroform as thermometric liquid offers the advantages of small specific heat, and small compressibility, compared with a pretty large expansibility (cf. Comm. N^0. 70 III § 3). The spiral contains about

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[1] Method II could not be applied to this screen To be able to apply this method the screens must be very clean and quite dry. In this instance it was impossible to fulfill the latter condition, for when the water was being drawn off from the jacket this lowest screen was kept moist by the water that remained behind since the level of the tap was but very little below the mark on the screen.

100 cc. and the thermometric vessel about 600 cc. of chloroform. By means of a tap Sp_3 the total mass of mercury present in the apparatus may be altered.

The action of the apparatus is briefly this : The glass spiral regulates the temperature of the bath B just as the copper spiral did in the Plate of Comm. N^0. 70 III, while the large vessel C considerably diminishes small temperature variations. The thermometric vessel which presents a relatively small surface compared with its large volume is not sensitive to these variations. The same applies equally well to integral temperature variations. Should, for instance, a continuous rise in the temperature of the room cause the temperature of the vessel C to rise a little, then mercury will flow from the thermometer vessel through Sp_9 to the spiral, the regulating flame will become smaller, and water will enter the large vessel at a temperature that is lower but is still kept constant by the spiral, so that the absorption of heat by the walls of the large vessel is thereby to a great extent neutralised.

The second purpose for which the modifications were introduced is, as can easily be seen, also served For, when once the burners have been lighted the thermostat adjusts itself to a temperature that is practically determined by the quantity of mercury present in the apparatus. The utility of the apparatus is therefore greatly increased. To give an idea of the capabilities of the apparatus temperatures taken on some of the measuring days are given below. The temperature was taken immediately before allowing the water to flow into the manometer jacket.

	12 h. 15 m.	12 h 45 m.	2 h. 15 m.	3 h. 5 m.	4 h. 55 m.
March 22nd 1911	16 04	16.07	16.07	16.07	16.07

	3 h 40 m.	3 h. 55 m.	4 h 20 m.	4 h. 45 m.	5 h. 25 m.	6 h.
March 30th 1911	19.00	19.00	19.00	19 00	19.00	19.05

So that the temperature as can be seen remains for hours at a time constant to less than 0.01°.

How far this constancy of the temperature can be utilised to keep the temperature of the volumenometer constant depends upon the constancy of the room temperature: its heat insulation however can still be improved If sufficient care is taken to keep the room temperature constant, one is usually succesfull in keeping the gradual change of the temperature of the volumenometer to within 0°.03 per hour [1]), and any single temperature measurement remains certain to 0°.02.

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[1]) For the comparison of mercury columns as in Table II constancy to within 10 times this value will be sufficient.

W. J. DE HAAS. "Isotherms of diatomic substances and their binary mixtures. VIII. Controlmeasurements with the volumenometer".

Pl. I.

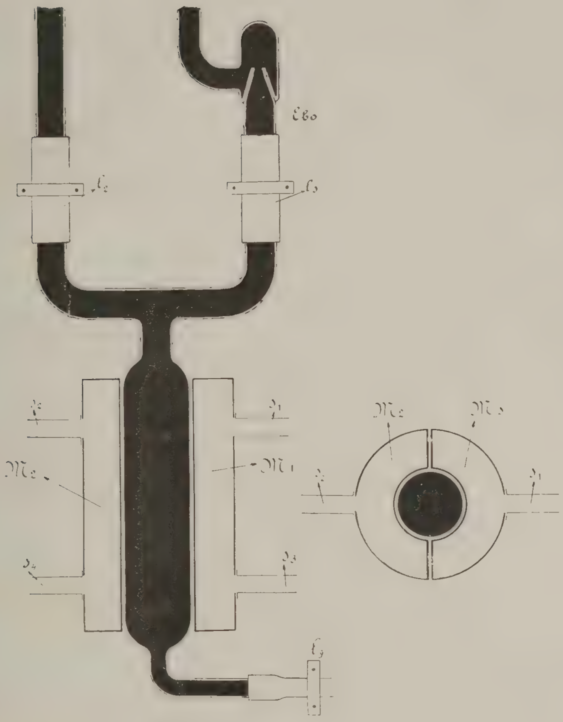


Fig. 1.

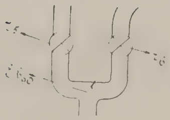


Fig. 2.

Communication No. 121a.

W. J. DE HAAS. "Isotherms of diatomic substances and of their binary mixtures. VIII. Controlmeasurements with the volumenomoter".

Pl. II.

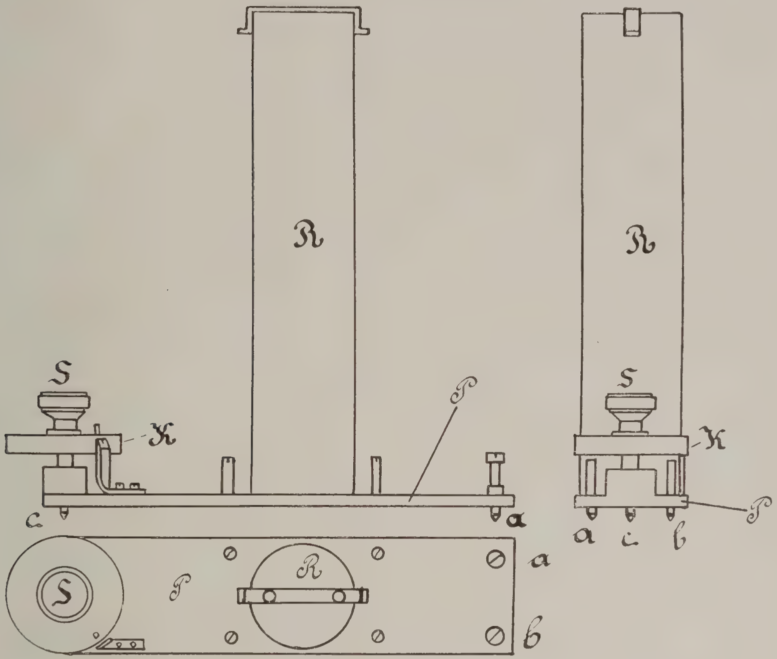


Fig. 1.

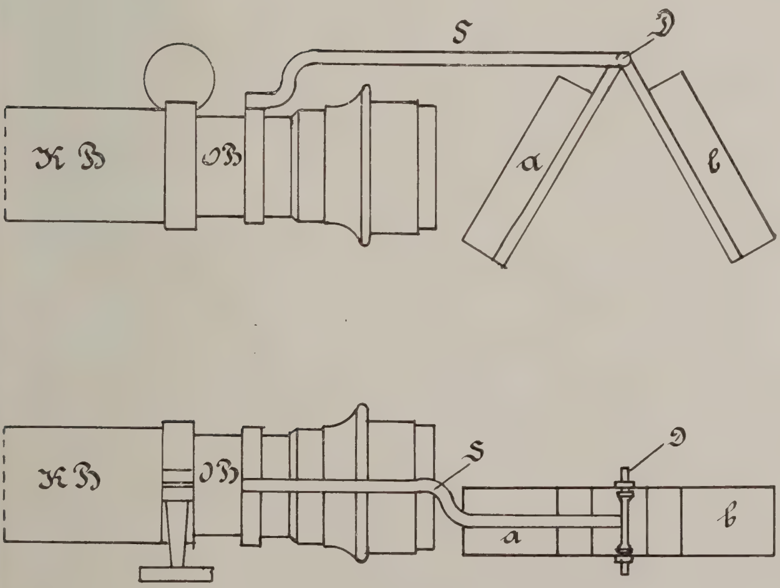
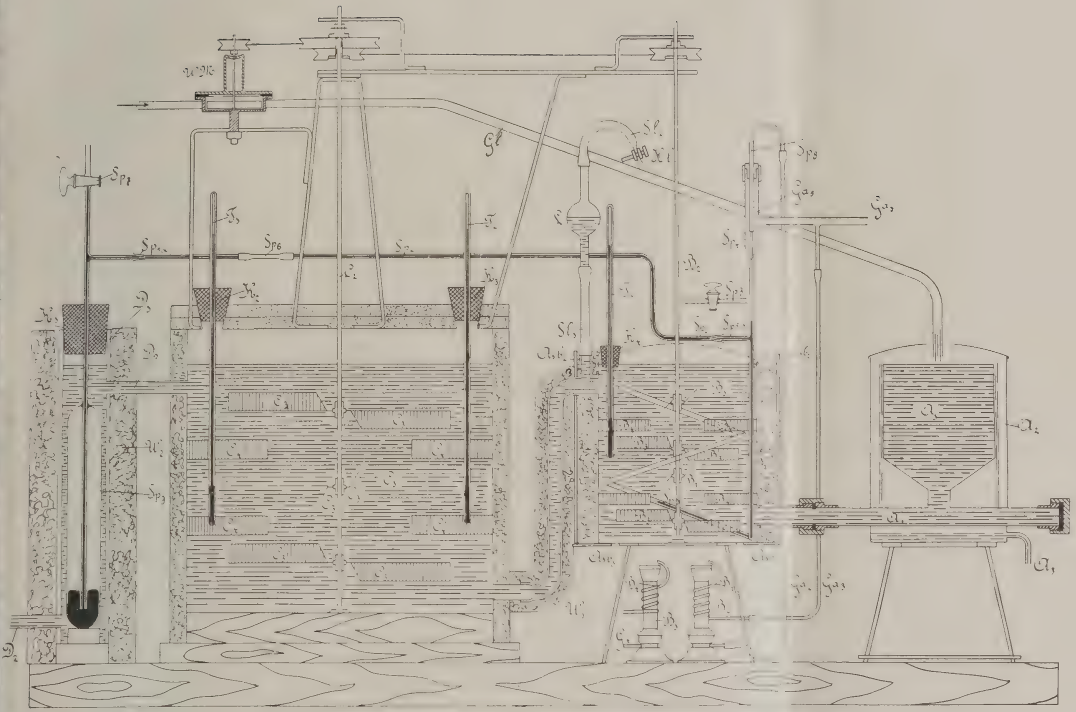


Fig. 2.

Communication No. 121a.

W. J. DE HAAS. "Isotherms of diatomic substances and their binary mixtures. VIII. Controlmeasurements with the volumenometer".

Pl. III.



Communication No. 121a.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 121^b.

H. KAMERLINGH ONNES and **C. A. CROMMELIN**. "Isotherms of monatomic substances and of their binary mixtures. X. The behaviour of argon with respect to the law of corresponding states". (Continued). (*With a plate*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **27 Mei 1911**, p. 68—72).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and **C. A. CROMMELIN.** "*Isotherms of monatomic substances and of their binary mixtures. X. The behaviour of argon with respect to the law of corresponding states.*" (Continued).

§ 4. *Comparison of argon isotherms with those obtained from the mean reduced equation of state, and with those for isopentane.* Two tables which we have already published, one of them [1]) containing the individual virial coefficients for argon calculated from the experimental results, and the other [2]) the corresponding coefficients deduced from the mean reduced equation of state VII. 1 afford, on comparison with each other, a means of determining the behaviour of argon with respect to the law of corresponding states. Of this behaviour which finds expression in systematic deviations from VII. 1 we have tried in Plate I to give a comprehensive representation which seems to us a suitable manner of giving striking expression to the characteristic deviation of the reduced equation of state for the monatomic substance argon from the mean reduced equation for the normal substances in general and from that for isopentane in particular. [3])

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[1]) Comm. N^0. 118*b* Table II.

[2]) Comm. N^0. 120*a* Table I.

[3]) With reference to the list of values of f published on page 1019 of our previous paper (IX of this series, Comm. N^0. 120a) we may remark that these values were obtained by substituting the vapour pressures and the corresponding temperatures along with T_k and p_k of Comm. N^0. 115 in the VAN DER WAALS vapour pressure formula, and that in these values of f in the neighbourhood of the critical temperature errors of observation are magnified. To diminish the influence of observation errors upon the deduction of the course of f in the neighbourhood of the critical temperature the observations can be adjusted by means of a vapour pressure formula which is in good agreement with the real values, and from these smoothed values the value of f for every temperature may be calculated. This

Our previous diagram [1]) referred to a much smaller region of temperature than that embraced by the present one for it extended only from $\log \mathfrak{t} = 0$ to $+0.06$, and from $\log \lambda\mathfrak{v} = -1.8$ to -3.2. For the construction in the region above the critical temperature and in the region of unsaturated vapour of the diagram now given we may refer to § 2 of our previous paper. In these regions percentage [2]) deviations of pv from the values of pv obtained from VII. 1 are again plotted as functions of $\log \lambda\mathfrak{v}$ and arranged according to $\log \mathfrak{t}$. In the liquid region deviations in v at any temperature occasion very much larger deviations in pv, so much so that it would be impossible to show at the same time in a single diagram percentage deviations of pv in both the liquid and gaseous states. This difficulty has been avoided by taking Δv [3]) in percent of v [4]) calculated from VII. 1 in the region of small volumes [5]) as the deviations and plotting these as ordinates taking the corresponding line belonging to $\log \mathfrak{t}$ as abscissa axis.

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was the treatment adopted in Comm. N^0. 115, and for the critical point was then deduced $f = \frac{T_k}{p_k}\left(\frac{dp}{dT}\right)_k = 5.712$, which by using common logarithms in the vapour pressure formula as was done in Comm. N^0. 120a becomes 2.481; it must therefore be concluded that f between — 140° C. and the crititical point gradually increases in value from 2.415 to 2.481 or in natural logarithms from 5.561 to 5.712.

In this connection compare J. D. VAN DER WAALS, Proc. April 1911.

[1]) Comm. N^0. 120*a*.

[2]) 1 % corresponds to 2 mm. on the diagram.

[3]) Comm N^0. 71 § 6 and No. 74 § 4.

[4]) The symbol Δ will always be used to represent the difference between the observed value of a magnitude and the corresponding value deduced from VII. 1, e. g. $\Delta v = v_O - v_C$.

[5]) The evaluation of $\frac{\Delta v}{v}$, $\Delta(pv)$ having already been calculated is made in the following practical fashion: the quantity $\frac{d\,(\log v)}{d\,(pv)}$ is evaluated along the isotherms either by drawing tangents or by linear interpolation between the observations or by calculation from VII. 1; of the three methods the last is to be preferred. It is now assumed that the VII. 1. isotherms are practically parallel to the experimental isotherms — indeed, the last

In one strip of the diagram going from the critical state towards higher temperatures and larger volumes the graphs of $\frac{\Delta(pv)}{pv}.100$ and $\frac{\Delta v}{v}\,100$ are the same. On the larger volumes side of this strip the first method was chosen and on the smaller volumes side the second. It appears that in this way a comprehensive representation of the differences between the isotherms may be obtained for the whole region [1] [2].

Only boundary curves and diameters [3] obtained from experimental data are shown, and those which would be obtained from VII. 1 are omitted. The reason for this is that the determination of these curves from VII. 1 necessitating a very prolonged calculation has not yet been completed.

The boundary curve for argon has been lengthened on the liquid side by means of Baly and Donnan's observations in the neighbourhood of the boiling point.

We mentioned in our former paper that the introduction of the

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method is based upon this hypothesis — and we may, therefore, write

$$\frac{d\,(log\ v)}{d\,(pv)} = \frac{\Delta\,(log\ v)}{\Delta\,(pv)}$$

(see note 4 on page 4). This assumption is correct to sufficient approximation and is legitimate at all events where it is only a question of giving expression to systematic changes in the differences, so that rigorously care has to be taken only that they are always subjected to the same perfectly definite treatment. The above now becomes

$$\frac{d\,(log\ v)}{d\,(pv)}\,.\,\Delta\,(pv) = log\left(1 + \frac{\Delta\,v}{v}\right)$$

from which $\frac{\Delta\,v}{v}$ is easily obtained.

[1] Since observations upon argon in the region of great densities are not yet available we shall not further discuss the exact shape of this strip.

[2] In our choice and development of this manner of presenting the results we have gratefully taken advantage of the experience gained by Mrs. van Rheedt-Dortland, née Sillevis in earlier calculations and constructions.

[3] For abscissae of points on the diameters we have taken values of the quantity $log\,\dfrac{2\lambda}{v_k\left(\dfrac{1}{v_{liq.}} + \dfrac{1}{v_{vap.}}\right)}$ in which volumes are expressed in terms of the theoretical normal volume as unit.

quantity $\lambda \mathfrak{v} = \frac{p_k}{T_k} v$ ¹) enabled us to leave entirely out of account the value of the critical volume deduced for isopentane from the diameter law, and for argon from the equation $\left(\frac{\partial p}{\partial T}\right)_{v.k.} = \left(\frac{dp}{dT}\right)_{c.\,ex.\,k.}$ The same principle has been also utilised in drawing the whole of the accompanying diagram with the exception of the critical points themselves (marked k on the diagram) which here appear as points of contact between the experimental boundary curves and the critical temperature axis.

From the diagram it is quite evident that the various differences between argon and ordinary normal substances, in particular isopentane are systematically connected over the whole region, and that we must ascribe the appearance of this difference graph to a definite cause common to the various deviations. We may obviously look for this cause in the hypothesis that the monatomic argon molecule is less compressible than the poly-atomic isopentane molecule. This circumstance is clearly shown at the smaller volumes. Along the whole of the liquid branch of the boundary curve the argon volume is greater than the isopentane volume, and this is in agreement with the values which we found for K_4 and a_M viz.

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¹) The quantity $\lambda = \frac{p_k v_k}{T_k}$ (see Comm. No. 71) which was used in our former paper is connected with the quantity $K_4 = \frac{RT_k}{p_k v_k}$ by the simple relation $\lambda = \frac{R}{K_4}$. The property that $\frac{RT_k}{p_k v_k}$ is from the point of view of the law of corresponding states an invariant was first utilised in Comm. N⁰. 59*a*, while in Comm. N⁰. 65 it was first applied to mixtures. In Comm. N⁰. 66 it appeared as C_4 along with the quantities $C_1\, C_2\, C_3$ which had been introduced before, and which, from the point of view of the law of corresponding states, are also invariants. In Comm. 120*a* and Comm. 117 K_4 is written for C_4 to prevent confusion with the coefficient C of the general equation of state, and in future this change will be continued.

Comp. also Ph. A. Guye, Ann. d. Chim. e. d. phys. (6), 21, 211, 1890 and Arch. d. Sc. phys. e nat. (3), 23, 204, 1890.

$$\begin{aligned} K_4 \text{ (argon)} &= 3.28 \text{ while} \\ K_4 \text{ (isopentane)} &= 3.73\,; \\ a_M \text{ (argon)} &= 0.9027 \text{ while} \\ a_M \text{ (isopentane)} &= 0.8923 \end{aligned}$$ [1].

The most obvious explanation of these larger values for argon is to ascribe them to the absence in argon of the usual compressibility of the molecules of normal substances [2]. Indeed, taking for the moment the VAN DER WAALS isotherms, $\lambda = \frac{Rv}{8b}$, that is to say, a constant (i. e. independent of the temperature) displacement of *log* $\lambda\mathfrak{v}$ means that b is increased or decreased in a definite ratio Looked at from this point of view the accompanying diagram gives immediate experimental expression to the fact that the argon molecule is less compressible than the molecule of an ordinary normal substance. From this it is probable that the differences between the values of K_4 and of a_M must also be ascribed to the same cause.

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[1] It is worth noting the appearance of the vapour branch for argon which, in this diagram, almost coincides with that for isopentane. If we imagine a reduced GIBBS surface on the one hand for argon, on the other for isopentane, then for argon the liquid crest is displaced towards the side of larger volumes, and in the vapour region the surfaces take a different form on account of the deviations of the isotherms. The two causes, therefore, in conjunction with a raising of the liquid crest must so operate that a coincidence of the vapour branches of the boundary curves is obtained.

[2] As will be shown in an article by H. KAMERLINGH ONNES and W. H. KEESOM on the equation of state and its graphical treatment which will shortly appear in the *Encyclopaedie der mathematischen Wissenschaften*, differences between the surfaces of state for various substances such as have here been found to exist between argon and isopentane may also be brought about by a difference in the distribution round the molecule of the mean attraction potential, for example, by a difference in the ratio between the *halving distances* (i. e. distances over which the potential is diminished by half) to the radius of the molecule supposed spherical with which, according to the latest considerations put forward by VAN DER WAALS, should be connected a varying degree of apparent association On the other hand such a difference in distribution of the attraction potential could depend on a difference in the molecular shape; it might, for instance, be that with spheroidal molecules either prolate or oblate the possibility of closer packing may give rise to an overlapping of more concentrated parts of the corresponding fields of force, which would conduce to the development of a greater attraction virial, (and consequently also to a higher value of the critical temperature).

Cf. also Comm. N°. 119.

The question still remains if we are here dealing with an actual smaller molecular compressibility, or with phenomena which would result from appreciable deviations from true spheres in the shape of the molecules, which could therefore, at higher densities, be packed more closely than would be possible with spheres, of which the radius is equal to the average radius which is to be ascribed to the molecules in the gaseous state. For isopentane, then, a prolate molecule might be assumed. But since carbon dioxide also belongs to the substances under consideration which agree well with VII. 1, and as it is not necessary to assume for it a molecule which is either particularly prolate or particularly oblate, the diagram seems to show that in this case it is really molecular incompressibility with determines the behaviour of argon.

Erratum Communication N⁰. 121*b*.

p. 26 line 1 from the bottom: for with read which.

H. KAMERL of their binary mixtures.

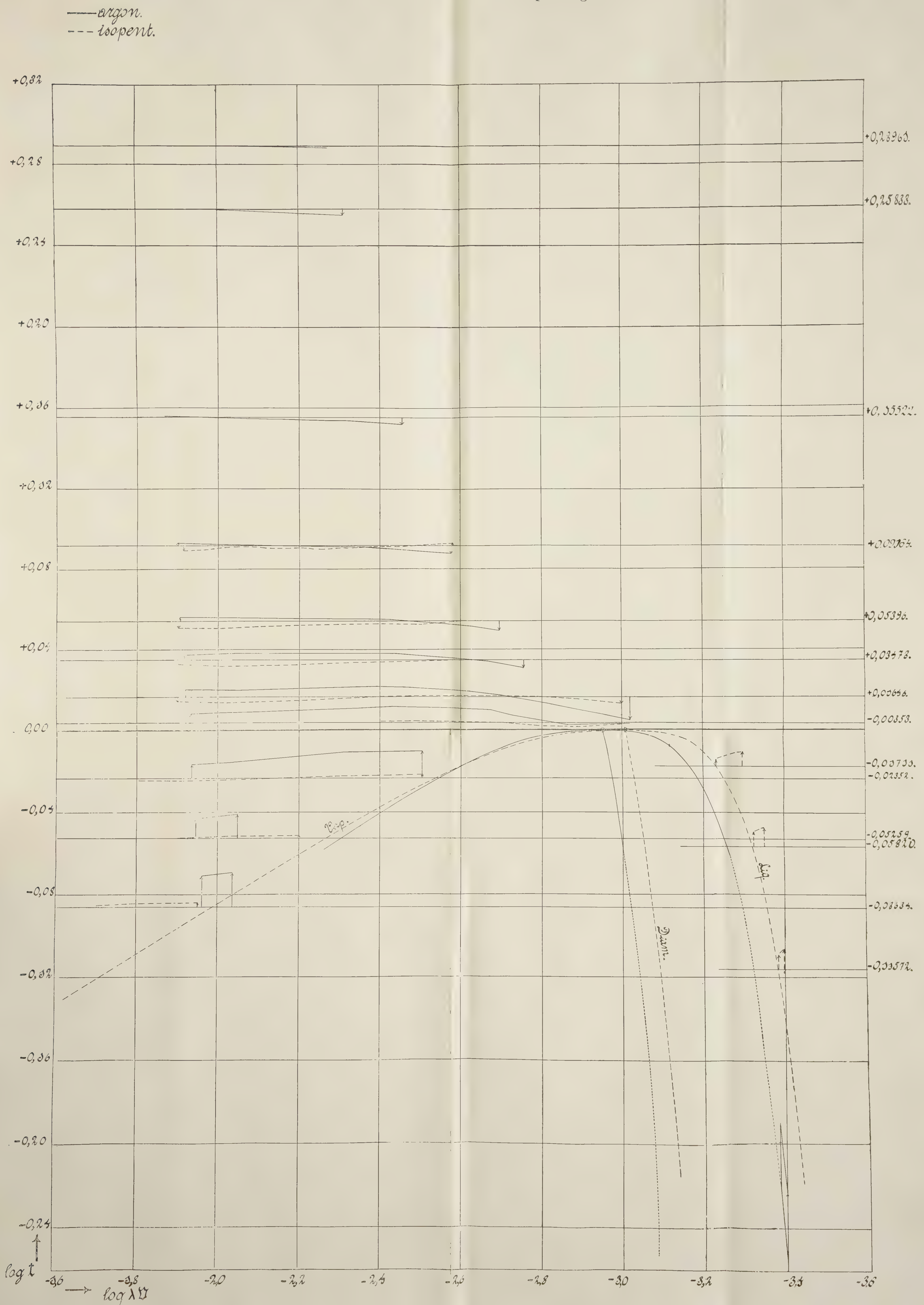
X. The

PLATE I.

——argon.
---isopent.

-0.82

H. KAMERLINGH ONNES and C. A. CROMMELIN. "Isotherms of monatomic substances and of their binary mixtures X. The behaviour of argon with respect to the law of corresponding states." **PLATE I.**



Communication No. 121b.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 121c.

H. KAMERLINGH ONNES and **C A. CROMMELIN**.
"Isotherms of monatomic substances and of their binary mixtures. XI. Remarks upon the critical temperature of neon and upon the melting point of oxygen."

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **27 Mei 1911**, p. 73—74).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and **C. A. CROMMELIN**. "*Isotherms of monatomic substances and of their binary mixtures. XI. Remarks upon the critical temperature of neon and upon the melting point of oxygen.*"

For some time past we have been busy with an investigation of the equation of state for neon in which a place of importance is taken by the isotherms for the temperatures which are repeatedly used with liquid oxygen in our cryostat, viz. —182° C. to —217° C. It is obvious that for the purpose of this branch of the investigation one should be able to take advantage of a knowledge of the critical temperature.

Before, therefore, proceeding to determine a series of isotherms which would be specially arranged with a view to the deduction of the critical temperature from these isotherms — which is the obvious method of obtaining a reliable estimate when the direct determination cannot be made with a bath of liquid oxygen — we have first ascertained if the critical temperature of neon lies above or below the melting point of oxygen. Such an investigation is necessary because the critical temperature of neon is not yet definitely known, and the estimates which have been made of it differ widely. TRAVERS, SENTER and JACQUEROD [1]), who start with the assumption that the critical temperature of neon must lie below — 213° C. obtain the value — 223° C., while A. O. RANKINE found a short time ago from two different methods the two values — 210°.4 C. [2]) and — 212°.0 C. [3]).

For the melting point of oxygen ESTREICHER [4]) gives — 227° C.

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[1]) M. W. TRAVERS, G. SENTER and A. JACQUEROD, Phil. Trans. A. 200, 105, 1902.

[2]) A. O. RANKINE, Proc. R. S. A. 84 pg. 190.

[3]) A. O. RANKINE, Phil. Mag. Jan. 1911.

[4]) T. ESTREICHER, Bull. A. Sc. Cracovie. Dec. 1903.

Relying upon these data, therefore, one should be able to determine the critical constants for neon by using a cryostat containing oxygen cooled by means of liquid hydrogen to the neighbourhood of its melting point. Indeed, if RANKINE's estimates are correct we should be able to attain the desired temperature by means of oxygen boiling under greatly reduced pressure, by means of which temperatures are usually obtained down to about ± — 217° C.

Experiment has shown that both deductions are incorrect.

A cryostat [1]) consisting of a partly silvered vacuum glass and containing not only the piezometer reservoir full of neon but also a platinum resistance thermometer and a valved stirrer was filled with liquid oxygen and was connected to a BURCKHARDT vacuum pump of great capacity. To minimise as far as possible heat exchange with the surroundings this cryostat was surrounded by a vacuum glass containing liquid air.

When the pressure in the cryostat had been diminished to 1 mm. we noticed that the liquid oxygen was covered with a crust of solid oxygen. A small increase in the pressure caused the solid oxygen to distribute itself throughout the liquid in the form of small transparent pieces (crystals?). As long as these pieces were kept in continual motion in the liquid by means of the stirrer a constant temperature of — 218°.4 C. was observed. Gradual compression of the neon to 60 atm. did not give rise to any trace of liquid in the neon piezometer nor did a gradual expansion from 60 atm. to atmospheric pressure. From this we may conclude that the critical temperature of neon lies at least some degrees below — 218° C., and that therefore the determination of the critical temperature had, in the meantime, better be made from the isotherms below — 200° C.

The result obtained for the melting point of oxygen is surprising. The difference between our value [2]) and that given by ESTREICHER can, however, be simply explained from the description of his experiment given by ESTREICHER in which he himself moreover declares that it is quite possible that his result lies somewhat too low. In his experiment half of the helium thermometer reservoir was in oxygen frozen solid over liquid hydrogen. It is quite probable that the temperature of that solid phase lay much lower than the true melting point of oxygen.

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[1]) Comm. N⁰. 83.

[2]) We hope to shortly communicate the results of a determination more accurate than this preliminary measurement.

We gratefully acknowledge our indebtedness to Mr. G. HOLST who was kind enough to undertake the measurement and calculation of the above temperatures.

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COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 122a.

H. KAMERLINGH ONNES and **ALBERT PERRIER**. "Researches on Magnetism. III. On Para- and Dia-magnetism at very low temperatures".

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **27 Mei 1911**, p. 75—81).

Eduard IJdo — Printer — Leiden.

H. KAMERLINGH ONNES and **ALBERT PERRIER.** "*Researches on Magnetism.* III. *On Para- and Dia-magnetism at very low temperatures*".

§ 1. *Introduction.* In an earlier research (Comm. N°. 116, April 1910) we investigated the magnetisation of oxygen down to temperatures close to the freezing point of hydrogen, and we found deviations from CURIE'S law which seemed to us to be connected with the problem as to how far the electrons which occasion magnetic phenomena are frozen fast to the atoms when the substance is cooled to very low temperatures [1]. This made it very desirable to extend the research, especially as far as hydrogen temperatures were concerned, to other paramagnetic substances which follow CURIE'S law at ordinary temperatures. If, as we found to be the case, it were found that deviations of the same character as those for oxygen were also encountered with these substances, it might well be assumed that such deviations, and also, should they be connected with the freezing of the electrons, this freezing itself would lie in the very nature of paramagnetism. In that case there would hold for every substance, as was shown in Comm. N°. 116 to be the case for oxygen, a more general law than CURIE'S which only within a definite temperature region would not differ appreciably from CURIE'S.

After we had been engaged upon an investigation in this direction for a considerable time its importance increased considerably from two different points of view. In the first place came the discovery by WEISS [2] of the magneton as forming a part of all magnetic atoms. Should the deduction advanced by WEISS that the molecular magnetisation of different substances can be expressed as whole multiples of the magneton hold for all temperatures, this would, because it supposes that the constant of CURIE is accessible, entail the validity of a law which gives the means to determine this constant, further allowance having to be made only for sudden changes in the number of magnetons or in the number of degrees of freedom. Certain of our measurements appear to be incompatible with exclusively discontinuous changes, for they even seem to indicate that gradual changes take place. Should this be the case, it is possible that deviations of the values of the magnetisation from those values which WEISS's theory would lead us to expect could be eliminated by means of corrections which our knowledge of these gradual changes would enable us to apply. And if it should appear from further investigation that all deviations could be explained by discontinuous changes then the knowledge of the law according to which these discontinuities occur is, by the discovery of the magneton, made a matter of the highest importance. However the case may be, we shall, in speaking of the deviations from CURIE's law mean both continuous and discontinuous changes

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[1] This idea of which repeated use has been made in former Communications (cf. WEISS and KAMERLINGH ONNES, Comm. N°. 114, Febr. 1910 p. 9 note 1) did not appear to be applicable to the case of ferromagnetic substances (loc. cit. p. 9) as the temperature sank to the freezing point of hydrogen. Our experiments give rise to the further question as to how these substances would behave when the temperature was lowered still further.

[2] P. WEISS, C. R. 152 (1911) p. 134, 222, 309, also Arch. de Genève, May 1911.

In the second place the rather indefinite notion of the "freezing of the electrons in the atoms" has taken a more definite form since it was found (Comm. N°. 119, Febr. 1911) that the electrical resistance of pure metals disappears in liquid helium and that this can be ascribed to the coming to rest of vibrators of definite frequencies which are in radiation equilibrium according to PLANCK's formula. The freezing of the electrons which we mentioned in connection with the magnetisation of oxygen may also be looked for in the coming to rest of vibrators. Perhaps then it may also be that, in general, deviations from CURIE's law may be found to be connected with the extinction of the energy of the vibrators [1]) or of the circular motions according to the same formula and for the same reasons.

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[1]) From a friendly letter that just on going to press reached us from Professor WEISS, whose coming to Leiden gave the initial impetus to our magnetic researches, we learn that this idea has also occured to him.

In the present paper we shall confine our attention to a short résumé of the results which we have obtained up to the present in which we shall also include those referring to diamagnetic properties. In a further communication we hope to give the results of experiments upon which we are still engaged and at the same time further details of the experimental method. To attain a greater degree of certainty we used with the apparatus described in Comm. N°. 116 a new cryomagnetic apparatus with which it is possible to measure electromagnetically the forces exerted upon the experimental substance by a strong magnet, and with which it possible to place *at will* the experimental substance at the point of maximum attraction or repulsion as long as it occupies a space of small dimensions, or, if the experimental substance be in the form of a cylinder, to place it with its one extremity in the pole gap.

§ 2. *Numerical results*. The values given below are the results only of preliminary calculations. There are still to be applied some corrections which have not yet been fully investigated, but these in all probability will not, in the most unfavourable circumstances, exceed 2 $^0/_0$. The numbers given are, of course, mean values, $\varkappa$ is the specific susceptibility or the magnetisation coefficient per gram, and T is the absolute temperature.

TABLE I.

Crystallized Gadolinium sulphate $Gd_2(SO_4)_3$, $8\,H_2O$.[1]				
T.	$\varkappa . 10^6$	$\varkappa . T . 10^6$	Limiting values in kilogauss of the fields used.	Bath.
290.3	72.94	20880	5—12	Atmospheric.
20.33	1039	21120	3.5— 9	Liquid hydrogen.
17.01	1229	20910	3.5— 7.5	
13.91	1468	20460	„	

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[1] Prof. G. Urbain to whom we are greatly indebted has kindly placed this substance at our disposal as well as the Dysprosium oxide (table III) and some others of the group of rare earths which have not yet been studied. We record our most hearty thanks to him for his highly valued help.

TABLE II.

Crystallized ferrous sulphate (powdered)
(MERCK's very pure "for analysis")

T	$\chi.10^6$	$\chi.T.10^6$	Limiting values in kilogauss of the fields used.	Bath.
289.6	41.46	12010	9—16	Atmospheric.
77.45	154.5	11970	5—14	Liquid nitrogen.
64.24	186.1	11950	„	
20.33	555.4	11270	5 — 9	Liquid hydrogen
18.73	589.7	11050	„	
17.01	641.6	10920	„	
15.47	695.5	10720	„	
13.93	757.2	10540	„	

TABLE III.

Dysprosium oxide Dy_2O_3 1).

T	$\chi.10^6$	$\chi.T.10^6$	$\chi.\sqrt{T}.10^6$	Limiting values in kilogauss of the fields used.	Bath.
288.5	229.2	66140	—	7.5—14.5	Atmospheric.
170	374.6	63670	—	5.5—15.5	Liquid ethylene.
132.79	445.7	59200	—	5.5—14.5	
20.25	1915	38790	8620	2.5— 7.5	Liquid hydrogen.
17.94	2032	—	8608	„	
15.95	2173	—	8680	„	
13.93	2334	—	8715	„	

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1) Cf. table I note 1.

For insertion in Vol. XII, Nos. **121 – 132**.

Addendum Communication N^0. 122.

p. 7 line 6 from the top: add a note „cf. Comm. N^0. 132*e* § 13”.

The magnetisation coefficient at ordinary temperature is 7.5 % lower than that determined in Paris by Miss FEYTIS; this can probably be ascribed to the fact that we were unable to heat the substance to very high temperature immediately before the experiments; we hope to repeat this experiment later under more favourable circumstances.

TABLE IV.

Electrolytic bismuth (powder) supplied by HARTMANN and BRAUN and formerly used by E. VAN EVERDINGEN [1]).

T	$\chi.10^6$	Limiting values in kilogauss of the fields used.
291.1	— 1.272	12.5—18
20.32	— 1.551	
17.01	— 1.553	
13.93	— 1.545	

§ 3. *Deductions. Paramagnetic substances.* The order of sequence of the three paramagnetic substances has been purposely chosen. It is a striking fact that even down to 17° K. gadolinium sulphate remains in perfect agreement with CURIE'S law. It first begins to show a slight deviation in the direction of too small a susceptibility in the neighbourhood of the melting point of hydrogen. On the other hand the susceptibility of ferrous sulphate is inversely proportional to T down to 64° K. In a bath of hydrogen boiling under atmospheric pressure a deviation in the direction of a decrease is quite clearly noticeable, and this deviation increases rapidly as the freezing point of hydrogen is approached. And finally dysprosium oxide even between ordinary temperature and

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[1]) Cf. Suppl. No. 2 to Nos. 61—72.

170° K. shows a deviation of 4 % which gradually increases so far that in liquid hydrogen the susceptibility is only one half of $\frac{c}{T}$. Let us conclude our list by the addition of oxygen, remembering that this substance as well as ferrous sulphate and in all probability the two rare earths, too, follow CURIE's law at ordinary temperatures, and we can only conclude that probably the susceptibility of substances which obey CURIE'S law at ordinary temperatures will, in general, if the temperature be sufficiently lowered, increase more rapidly than they should in accordance with the $\frac{c}{T}$ formula, but that the individual temperatures at which the deviations become appreciable differ considerably for the different substances. It is noteworthy that, in the case of gadolinium sulphate, this temperature lies very low, and is probably only 15° K.

Concerning the behaviour of these substances at temperatures below that at which this deviation becomes appreciable, *liquid* oxygen can, in the first place, give us some information. In fact in this case another well defined law, viz. $\frac{c}{\sqrt{T}}$ has been found to obtain over a pretty wide range of temperatures (90° K. to 63° K.). At the lowest five temperatures reached the magnetisation coefficient of ferrous sulphate increases somewhat more rapidly than what would be in accurate agreement with this law, but it undoubtedly approximates to it. At the four hydrogen temperatures at which measurements were made dysprosium oxide follows the same law as liquid oxygen. Taking all this into account we are justified only in assuming that for all substances there exists a certain range of temperatures differing greatly for the different substances, for which this law to a high degree of approximation governs the dependence of susceptibility on temperature.

In the neighbourhood of 15° K. solid oxygen did not follow the $\frac{c}{\sqrt{T}}$ law, but deviated still more strongly from CURIE's law, and even showed a tendency to attain a constant value; further experiments which have not yet been completed confirm this result. As none of the three other substances have yet exhibited this phenomenon it still remains an open question if it is cha-

Erratum Communication N⁰. 122*a*.

p. 8 line 9 from the top: for more read less.

racteristic of oxygen only, or if one only needs to lower the temperature sufficiently to be able to invoke its appearance as a general property of all paramagnetic substances.

On the occasion of our research upon oxygen we remarked concerning the *theoretical explanation* of the increasing deviation with falling temperature that it might, amongst other causes, be due to *association* amongst the oxygen molecules. Some experiments which are still incomplete upon mixtures containing equal quantities of oxygen and nitrogen seem to exclude this explanation, but these experiments must be continued further to be quite conclusive. From the experiments which have already been concluded, however, we have sufficient reason for not reverting to this explanation in § 1.

We must further note that with none of the paramagnetic substances investigated have we been able to observe a decreasing susceptibility with increasing field, that is a *commencement of saturation* [1]).

Bismuth. It has been shown by CURIE and later confirmed by HONDA that for bismuth between ordinary temperature and the melting point the temperature coefficient of the magnetisation may well be represented by the formula

$$\chi_t = \chi_{20}\,(1 - \alpha\,(t - 20)).$$

The fact that at ordinary temperature we obtained an absolute value of the susceptibility which is somewhat smaller may be due to the presence of a small quantity of free iron which, on account of the intensity of the fields used, will have no influence upon the relative results; indeed, for various kinds of commercial bismuth which were not so pure as ours, CURIE found the same dependence upon temperature. The values which we obtained with our specimen may quite well therefore serve as the basis of deductions regarding relatives values. With $\alpha = 0.00105$, the mean of the values obtained by CURIE with samples which were not perfectly pure, extrapolating to 20°.3 K. we should obtain $\chi_{20 \cdot 3} = - 1.64 \times 10^{-6}$ which is a value rather greater than that given by experiment. It would therefore appear that the linear change of the magnetisation of bismuth does not go on as the temperature falls, and this result is also in agreement with the experiments of FLEMING and DEWAR, who only went as far as liquid air. The two values which we obtained in hydrogen boiling under reduced pressure seem to indicate that when the temperature sinks as low as this, the susceptibility becomes pretty well *independent* of the temperature; if the law of change were still linear at these temperatures then between 20°.3 K. and 13°.9 K. one should have to observe an increase of 0.7 %, while what was actually observed was rather a decrease.

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[1]) With regard to the difference that was found between the constants for the formula $\frac{c}{\sqrt{T}}$ for solid and for liquid oxygen (Comm. No. 116, April 1910, § 5), it may be remarked that crystallisation phenomena can influence them. The investigation of the problems referring to this point will be seen to be further complicated when we remark that on freezing oxygen transparent solid oxygen is first formed which, at lower temperatures, is transformed into an opaque mass.

Hydrogen. With a view to the determination of the corrections to be applied we made a measurement of the susceptibility of liquid hydrogen, the result of which probably deviates less than 10 % from the true value. This determination is rendered extremely difficult by the smallness of the density and of the volume-susceptibility of the hydrogen. We found for the volume-susceptibility $K = - 0.186 \times 10^{-6}$ and, taking DEWAR'S value for the density of liquid hydrogen 0.07 we find $\chi = - 2.7 . 10^{-6}$. Within the limits of experimental error this value agrees with that calculated by PASCAL ¹) $\chi = - 3.0 \times 10^{-6}$ from the organic compounds As we do not in the meantime propose to repeat this determination we feel that there is sufficient reason for us to communicate the result here.

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¹) P. PASCAL. Ann. chim. phys. (8) 19 (1910) p. 5.

COMMUNICATIONS

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 122^b.

H. KAMERLINGH ONNES "Further Experiments with Liquid Helium. D. On the Change of the Electrical Resistance of Pure Metals at very low Temperatures, etc. V. The Disappearance of the resistance of mercury".

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **27 Mei 1911**. p. 81—83).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES. "*Further Experiments with Liquid Helium. D. On the Change of the Electrical Resistance of Pure Metals at very low Temperatures, etc. V. The Disappearance of the resistance of mercury.*"

As mentioned in a former Communication (April 1911) I have made a more accurate examination of the resistance of pure mercury at helium temperatures, in which I have once more had the assistance of Messrs. DORSMAN and HOLST. The resistance was now measured with the differential galvanometer by the method of overlapping shunts (KOHLRAUSCH) and also by the method of the measurement of current strength and of potential difference. By this it was confirmed that at 3° K. the value of the resistance sinks to below 0.0001 times the value of the resistance of solid mercury at 0° C. extrapolated from the melting point. But from the present measurements it has also been ascertained that the actual value of the resistance is very much smaller than this upper limit which I was able to ascribe to it from my former measurements.

The value of the mercury resistance used was 172.7 Ω in the liquid condition at 0° C.; extrapolation from the melting point to 0° C. by means of the temperature coefficient of solid mercury gives a resistance corresponding to this of 39.7 Ω in the solid state At 4°.3 K. this had sunk to 0.084 Ω, that is, to 0.0021 times the resistance which the solid mercury would have at 0° C. At 3° K. the resistance was found to have fallen below 3×10^{-6} Ω, that is, to one ten-millionth of the value which it would have at 0° C. As the temperature sank further to 1°.5 K. this value remained the upper limit of the resistance.

The next step was obviously to look for the point at which the resistance first becomes measurable as the temperature is raised. The temperature of this point was found to be slightly more than 4°.2 K. at which the resistance was found to be 230 micro-ohms or one hundred thousandth of the resistance (solid) at 0° C. As the temperature was raised to that of the boiling point (4°.3 K.) the resistance rose once more to 0.084 Ω. This change took place more quickly than the rate of change to which the formula given in the December (February) Communication leads—exactly how much more quickly is not yet known but it certainly seems to increase very much more rapidly. A point of inflection which does not appear in the formula given — a formula which I regarded as incomplete also on account of the method by which it was deduced — seems to occur between the melting point of hydrogen and the boiling point of helium in the curve which represents the resistance as a function of T.

The more the upper limit which can be ascribed to the resistance remaining at helium temperatures decreases, the more important becomes the observed phenomenon that the resistance becomes practically zero. When the specific resistance of a circuit becomes a million times smaller than that of the best conductors at ordinary temperatures it will, in the majority of cases, be just as if electrical resistance no longer existed under those conditions. If conductors could be obtained which could be regarded as being devoid of resistance as long as their cross section was not excessively small, or conductors of the smallest possible sections, either cylindrical with diameters of the order of the wave length of light, or films of molecular thickness, whose resistance would be but small, if there had no more to be reckoned with the JOULE development of heat in increasing the current in a bobbin to exceedingly high values because the development of heat in a circuit of constant current strength could be made extremely small compared with the latent heat of vaporization of the liquid which can be used for cooling, — then further experiments in all possible directions would give the fullest promise, notwithstanding the great difficulties which are encountered when working with liquid helium. It is therefore all the more necessary to establish beyond all possibility of doubt the property of which advantage would be taken in such experiments. With this end in view modified measurements are now being made.

It is further worth noting that just as the resistance of constantin changed but little when the temperature fell from ordinary to liquid hydrogen temperatures so too the change is slight as the temperature sinks further to those of liquid helium. This property was utilised to obtain rough confirmation of the value of the latent heat of vaporization of helium which can be calculated from CLAPEYRON's formula using the data already published concerning its vapour pressure and vapour density. (Compare the above remarks as to the ratio between the JOULE heat development to the latent heat of the liquid which is used for cooling).

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No. 123.

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H. KAMERLINGH ONNES. "Further experiments with liquid helium. E. A helium-cryostat. Remarks on the preceding communications." (*With a plate.*)

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H. KAMERLINGH ONNES. — "*Further experiments with liquid helium.* E. *A helium-cryostat. Remarks on the preceding communications.*"

§ 1. *Introduction.* In the Jubilee volume presented in October 1910 to J. M. VAN BEMMELEN a description was given of an arrangement by means of which liquid helium had been successfully transferred from the apparatus in which it was prepared to another vessel in which the measuring apparatus could be immersed in liquid helium. Advantage was then taken of this arrangement to investigate how far liquid helium could be cooled before solidifying, and to reach the lowest temperature hitherto attained. But, as was pointed out in that paper, this arrangement did not appear to afford the requisite certainty in its action.

Experiments upon the electrical resistance of metals at helium temperatures and upon the thermal properties of helium were, therefore, again made (December 1910) by introducing the necessary apparatus into the chamber of the helium liquefier in which the liquid formed by the expansion of the gas collected. But, as long as a stirrer cannot be used in the helium bath, and with this arrangement its introduction would be a matter of the greatest difficulty, one cannot be sure of the uniformity of the temperature of the bath which, nevertheless, is a *sine qua non* for accurate temperature determinations. There was consequently urgent need for the construction of a cryostat [1]) which, although still closely connected with the liquefier, would yet allow the apparatus which one wished to place in the helium bath to be introduced and still have free and independent exit from above. In the present paper a description is given of a cryostat which fulfills the necessary conditions. With this cryostat various experiments have been made including those upon the disappearance of the resistance of pure mercury (Comm. No. 120 and Comm. No. 122*b*).

Now that this cryostat is available it is possible to measure the resistance of a mercury thread (CALLENDAR's bridge method, ordinary differential galvanometer method, method of overlapping shunts, measurement of fall of potential and current strength) whose four leads connecting with the measuring instruments are also (glass tubes filled with in the lower part solid) mercury up to the point at which ordinary temperature is reached Moreover, the difficulties attending an investigation of phenomena connected with electrical conduction are diminished, and in this connection an investigation is proceeding with a view to ascertaining how far one can, in measuring all kinds of very small potential differences, take advantage of the increase of sensitivity experienced by the current carrier (e.g. fixed coil [1]), suspended coil, current circuit or string) of the galvanometer when brought to the temperature of liquid hydrogen. Finally, one can attempt to obtain baths giving temperatures between the boiling point of helium and the melting point of hydrogen, which must be regarded as of the highest importance for resistances (and perhaps for specific heats as well), and which are essential for an accurate determination (already once unsuccessfully attempted) of the critical temperature of helium [2]).

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[1]) Cf. also Comm, No. 119 A § 6,

A short description of this cryostat, therefore, is desirable.

§ 2. *Description of the apparatus.* The chief difference between this and the apparatus described in the VAN BEMMELEN-Jubilee volume lies in the separation of the helium liquefier from the cryostat chamber by a valve, and in the siphoning over of the liquid helium through a cooled siphon. For the rest, the apparatus on the one side resembles the apparatus described in the VAN BEMMELEN volume, and on the other the liquefier with enlarged reception chamber described in Comm. No. 119. Reference may be made to Comm. No. 119 for a description of all that is common to the earlier and the later apparatus; the same letters are used to indicate identical parts, while, where one of the parts has been modified, the letters are distinguished by accents. As in Comm. No. 119 reference must be made to the earlier Communication for a detailed description of the parts common to the helium liquefier there described and that given in Comm. No. 108, while the plates given in Comm.'s No. 108 and No. 119 should be consulted along with that given with the present paper [1]).

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[1]) When thus cooled the resistance of a fine wire coil is diminished to that of a thick wire coil.

[2]) For a criticism of the *thermal properties of helium* an accurate knowledge of this temperature is essential. In this connection we may remark that circumstances other than those brought forward in § 6 of Comm. No. 119 may influence the deviation of helium from ordinary normal substances in the sense opposite to that in which associated substances deviate from them. An increase in the elongation of the vibrators would bring the attracting particles closer to the surface of the atoms and this could lead to an increased association at higher temperatures. But, in particular, a peculiarity in the equation of state of helium, ascribed to a particular change of a and b, may just as well be brought about by the non-appearance of changes occurring in ordinary normal substances (and perhaps too in substances such as argon and oxygen whose critical temperature is not yet too low) which had not been allowed for in the examination of the changes

The silvered siphon tube *Eah* (see accompanying figure) which transfers the liquid helium from the vacuum glass Ea'' of the liquefier in which it collects to the vacuum glass of the cryostat S_7 — the cryostat glass — is fused to the under part of the vacuum glass $Ea''h_1$. The lower portion of the liquefier's vacuum glass as well as the rising limb of the siphon Eah_2 are surrounded with liquid air in S_a from which they are separated by a german silver case S_1 cemented and consequently immovably attached to the liquefier glass at S_{11}. To this case the ring S_4 which carries the cryostat glass S_7 is also fixed immovably. When the cryostat glass with its rubber ring S_5 is attached to this, and the cover S_6 with its rubber ring S_{61} is placed over the cryostat chamber, this case forms with the connecting tube S_3

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undergone by their a and b. For it is the comparison of helium and ordinary normal substances, that is regarded. An increase in the value of b for helium would, therefore, correspond with the total or partial absence of a diminution of b (compressibility) of normal substances, and similarly an increase of a with temperature for helium would correspond with the absence of an increase in a at temperatures down to those usually reached with ordinary normal substances.

(Cf. too the note on the compressibility of argon atoms in Comm. No. 121*b* by KAMERLINGH ONNES and CROMMELIN, p. 25 note 2)

[1]) In the construction of this cryostat as well as of the apparatus placed in it during the various experiments I owe much to the skill and ingenuity of Messrs. FLIM and KESSELRING, instrument maker and glass blower respectively at the Cryogenic Laboratory.

and the cryostat glass S_7 one closed whole. The same method of connecting by means of rubber rings as was used in the earlier cryostats was again employed with the liquefier at S_{12} above the cemented junction S_{11}, and this connection also provided with a safety envelope thus ensuring an air-tight sealing of the whole enclosed space. A helium thermometer whose german silver reservoir N_{b1} is placed in the liquid helium space indicates the accumulation of liquid helium which may be transferred to the cryostat chamber; its steel capillary Nb_2 passes along by the spiral A of the helium liquefier and is connected to a stem Nb_3 and a barometer tube; this thermometer is placed alongside the thermometer S_5 which indicates the level of the liquid in the hydrogen chamber of the liquefier N and Na (cf. the plate of Comm. No 119).

Along the upper end of the siphon Eah_2 is laid a copper capillary Eal through which liquid air is flowing; this capillary is wrapped up with the siphon tube in a layer of insulating material; by this means it is ensured that when the liquid helium flows quickly over it takes up but little heat. At the extremity of the siphon Eah_5 which opens into this cryostat glass is a valve Eak, consisting of a stopper plate Eak_1 which turns about a horizontal axis and is pressed against the opening of the vacuum tube by means of the large-pitched worm gear Eak_2. The worm is operated from above the cover of the cryostat by turning the handle Eak_3 to which is attached the shaft Eak_5 (made partly of glass) passing through the stuffing box Eak_4.

The stirring arrangement consists of a german silver pump Sb, with valved piston Sb_1 and outlet valves Sb_2; by means of a wire Sb_4 and a soft iron cylinder Sb_6 inside the glass tube Sb_7 the piston follows the course of a magnet Sd which is moved up and down by an electric motor [1]). By this means a powerful circulation is obtained.

Only the upper portion of the cryostat glass is silvered. At the level of the inlet valve the silvering ceases, so that one is able to control the action of the valve and to observe the level of the liquid meniscus in the cryostat glass. A vertical strip on each side of the vacuum glass $E''b$ which contains liquid hydrogen and surrounds the cryostat glass is left unsilvered so that the position of the liquid helium in the cryostat glass may be seen. The vacuum glass $E'''c$ with liquid air which protects the liquid hydrogen is treated in the same way. Vaporization is chiefly due to entrance of heat from above by conduction and by absorption of radiation from uncooled or insufficiently cooled portions of the apparatus (e. g. cover, resistance thermometer leads, etc.). The radiation, too, which is admitted through the transparent parts of the walls as well as the radiation from above can be absorbed by objects which are in contact with the liquid helium (this seems to be particularly the case with the opaque or metal parts of the apparatus), and can give rise to considerable evaporation [1]. For many experiments the rapid evaporation occasions great difficulty.

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[1]) It is peculiarly charming to see this little pump ejecting the light liquid over its upper edge when the level of the liquid helium sinks a little below it.

In the case represented by the accompanying Plate (experiments of April 1911) the cryostat contains *a.* the helium thermometer Th_3'' (with capillary Th_2''); *b.* the gold resistance thermometer Ω_{Au} (an insulated gold wire wound on a glass cylinder); *c.* the mercury resistance Ω_{Hg} [2]. To make it possible for the mercury to solidify and liquefy again without division and without injuring the glass the last resistance consists of a series of ⋃-shaped glass capillaries filled with mercury arranged in a circle and connected by expansion reservoirs; there are four platinum leads for coupling it to the measuring instruments.

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[1] The whole of these *radiation and absorption phenomena at extremely low temperatures* lead to the conviction that in bringing a measuring instrument that receives radiation to a low temperature a wide field of investigation is made easily accessible. In this connection it may be mentioned that according to the well known formula $\lambda_m T=0.294$ cm. deg., at the lowest helium temperatures λ_m becomes approximately 2 mm. (at the melting point of hydrogen a value of 0.2 mm. is already realised); the heat radiation, therefore, given by the wavelength λ_m is almost identical with the actual HERTZ oscillations of small wave length (4 mm) realised by LAMPA. We may also mention that at 4° K. at which temperature vibrators of wave length 0.5 mm. which seem to play an important part in electrical resistance come to rest, λ_m becomes 0.7 mm. approximately.

[2] The estimate of the *frequency of the resistance vibrators in mercury* (which gave $a=30$, see Comm. No. 119 B, § 3 note 6 under table) was obtained by paying due attention to the fact that the situation of the chief points on the curve defining resistance as a function of temperature

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seemed to be determined by the melting point — a fact already commented upon in Comm. No. 99*c*. I thought it clearly suitable to apply the law of corresponding states to metals, which has been done repeatedly since, and to regard the melting point as a corresponding temperature. I also thought that when it was a question of concluding from elastic phenomena, the principle of mechanical similarity could well be applied, as I had already done in explaining the extended validity of VAN DER WAALS's law of corresponding states.

Metals, therefore, in corresponding states are regarded as mechanically similar systems the various properties of which, expressed in units depending upon length, mass and time, are, when in corresponding states, given by the same numerical values by using units which are obtained for each metal from its own fundamental units $[L]$, $[M]$, $[T]$. The natural units of mass and volume are the atomic weight M and the atomic volume, so that $[L] = M^{1/3} \rho^{-1/3}$ where ρ is the density. The particular unit of time for each metal is the reciprocal of the frequency here required, i. e. the period of the resistance vibrators. According to the dimensions $[L^2 M T^{-2}]$ of kinetic energy which determines temperature, we derive from the corresponding melting point temperatures θ_s and θ'_s and from the expression

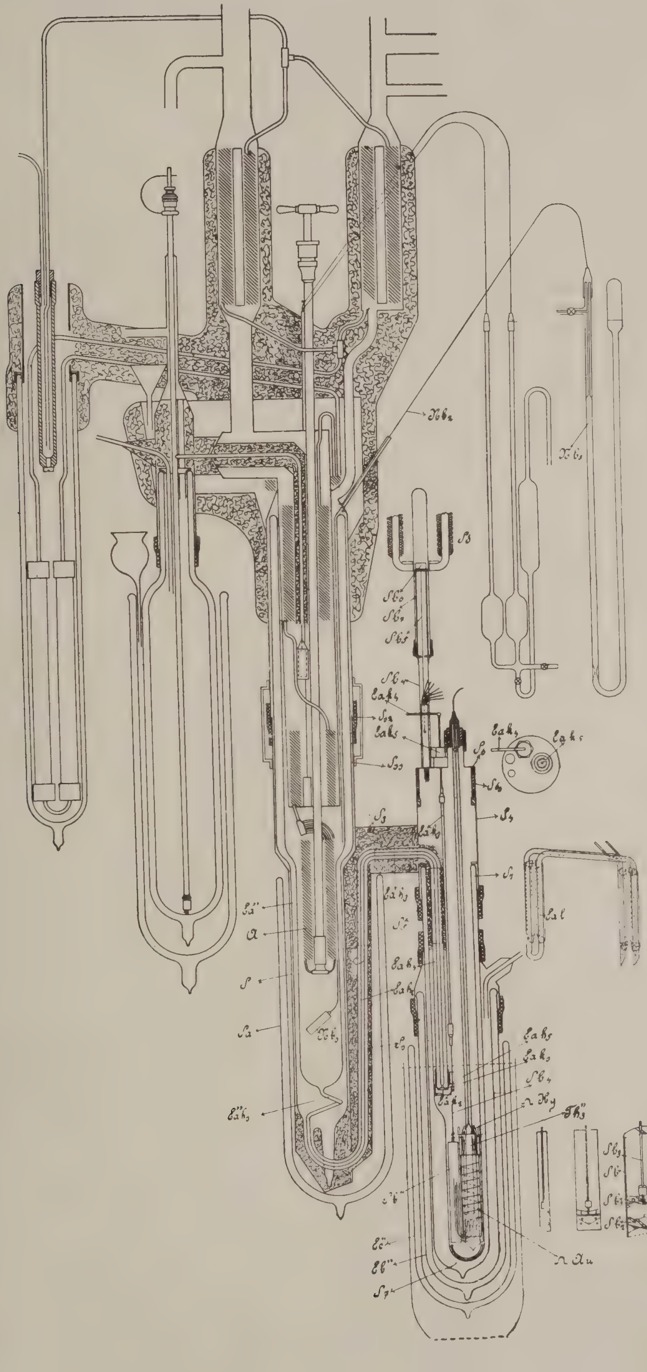
$$[T] : [T'] = [L] M^{1/2} \theta_s^{-1/2} : [L'] M'^{1/2} \theta'^{-1/2}_s =$$

$$= \rho^{-1/3} M^{5/6} \theta_s^{-1/2} : \rho'^{-1/3} M'^{5/6} \theta'^{-1/2}_s$$

that — taking the frequency for lead such that $a = 54$, — the frequency for mercury should be such that $a = 37$. As comparison with platinum would give a value 47, we can regard the results of this method as only a rough approximation, and a further reduction to 30 which promised to give better agreement seemed quite permissible.

I have more recently seen a formula for the frequency deduced by LINDEMANN as far back as 1910 (Physik. Zeitschr.) from more specialized assumptions, from which the expression just given follows at once; this is not surprising since the principle of similarity may be applied to his assumptions. While I wish to take this opportunity — as I should have done in my first paper on the subject — of referring to these important calculations of LINDEMANN, it is perhaps fortunate that I had not seen them sooner, for they give $a = 46$ for mercury, while it was just from the estimate $a = 30$ that I was able to forecast that at some of the helium temperatures the resistance of mercury could be measured and at lower temperatures it would disappear, and it was this forecast that made experiments with mercury so particularly inviting joined with the prospect of working with a pure metal.

H. KAMERLINGH ONNES. "Further experiments with liquid helium. E. A helium-cryostat. Remarks on the preceding communications."



Communication No. 123.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

[illegible] UNIVERSITY [illegible]

N°. 124a.

H. KAMERLINGH ONNES and **ALB. PERRIER.** — „Researches on Magnetism. IV. On Paramagnetism at very low temperatures."

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **30 December** 1911, p. 803—807).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and ALB. PERRIER. — "*Researches on Magnetism.* IV. *On Paramagnetism at very low temperatures*".

(Communicated in the meeting of November 25, 1911).

§ 1. *Solid Oxygen.* In a former Communication (May 1911) we mentioned our suspicion that the susceptibility of oxygen follows a law at liquid hydrogen temperatures quite different from CURIE's law, which is obeyed at ordinary temperatures. A continuation of our attraction experiments has amply confirmed this suspicion. The susceptibility, indeed, remains practically unchanged as the temperature sinks from the boiling point to the freezing point of hydrogen, and we have even found clear indications that after becoming constant the susceptibility begins to decrease when the temperature is lowered still further.

In our experiments the oxygen was contained in a closed thick-walled glass tube, having an upper wider and a narrower lower end connected to the first by a capillary. The gas enclosed in the tube was at a pressure of about 55 atmospheres at ordinary temperature. The tube was suspended in the apparatus and was kept in an equilibrium position in exactly the same way as the tubes containing powdered substances in our former experiments and, as with those tubes, it was completely surrounded by the vessel which held the bath of liquefied gas. In the present experiments the lower portion of the tube was slowly cooled by pouring liquid hydrogen drop by drop into the vacuum vessel which served to hold the bath of liquid gas. In this way the oxygen was caused to freeze to a solid piece practically cylindrical in shape, filling the lowest part of the tube. To make measurements possible, this cylinder was placed in that part of the magnetic field where the attraction was a maximum. The correction to be applied on account of the influence of the glass, which was pretty considerable at very low temperatures, was obtained by control experiments with an evacuated tube. For the specific susceptibility we found the values given in Table I.

TABLE I.

Solid oxygen.			
A		B	
T	$\chi . 10^6$	T	$\chi . 10^6$
20°.3 K	54.3	20°.3 K	52.3
18.5	55.8		
17.0	54.6		
15.5	54.7		
13.9	50.8	13.9	49.1

The corrections which are still to be applied to these values are insignificant (about 1 %). In the Table, A and B refer to two different experiments (different freezings of the oxygen). The difference between the absolute values in Columns A and B can be explained by the fact that the practically cylindrical piece of solid oxygen (11 mm. long and 4 mm. thick) was not of exactly the same length in the two cases. But even so, what we are immediately concerned with is not so much absolute values as the ratios between the values for the same cylinder at different temperatures.

Our formula from Communication N°. 116 gives for liquid oxygen at —210° C. the much greater value

$$\chi_{63^\circ K} \cdot 10^6 = 288.$$

In the course of our present experiments we have actually been able by direct observation of the magnetic attraction during the melting of the oxygen cylinder to establish as a fact the existence of a considerable sudden change in the susceptibility of oxygen on melting and freezing. In Communication N°. 116 we concluded that such a sudden change must exist, but it now appears that the magnitude of this change is actually much greater (four times) than the value which we then estimated for it.

We cannot yet with certainty say how we are to explain the considerable difference between the values of the susceptibility of solid oxygen which we have now obtained by the attraction method and those which we got before by the method of the couple. We were just on the point of investigating this question more closely when we were obliged for particular reasons to postpone further experiments for a considerable time, so that we shall now content ourselves with giving the explanation which we consider the most probable. This tentative explanation is that solid oxygen possesses magneto-crystalline properties, which was not previously known and which we had no reason to suspect. If the magneto-crystalline anisotropy of oxygen — on the track of which our experiments should bring us if our explanation is correct — is somewhat considerable, the values of the susceptibility given by the method of the couple can depend to a considerable extent upon the positions taken up by the crystals on solidification. In this way chance could play a considerable part in the results. We have already obtained an indication that this is the correct direction in which we must look for the proper explanation, for, on repeating our measurements by the method of the couple we obtained great differences in the values of the susceptibility according to the manner in which the freezing of the oxygen took place. While we were at first of the opinion that the manner in which we carried out the freezing for our measurements by the couple method was the most suitable for our purpose, and that for correct results we need only attend to the necessity of filling the ellipsoid completely with solid oxygen, we now think, in view of our later knowledge, that it had rather the disadvantage of enforcing a definite distribution of crystals along the walls of the ellipsoid and of thus giving rise to a magneto-crystalline couple which was greater than the demagnetizing couple.

It is easily seen that the forces exerted in our recent experiments in a non-homogeneous field (always with small values of the susceptibility) depend to a much smaller extent upon the positions of the crystals than the couples exerted in our former experiments in a homogeneous field. And, on the other hand, both our observations during the process of melting and the correspondence between the values of the susceptibility given by the attraction method for three successive freezings lead us to the conclusion that, as regards the absolute values obtained, our later results should be taken in preference to the others.

The results obtained with the ellipsoid for the change of susceptibility between 20° K. and 14° K. do not conflict with those given by the attraction method, if a suitable correction is applied for the glass of the ellipsoid. To get an idea of the influence of the glass we give values for its susceptibility and its specific susceptibility in the following table.

TABLE II

Glass.		
T	$\varkappa . 10^6$	$\chi . 10^6$
290°K	< 0	< 0
78	2.8	1.2
20.3	12.1	4.9
13.9	19.0	7.6

The absolute values are only rough approximations, as the shape of the tube was very irregular, but as the correction for the glass was determined independently as a whole in the application of the attraction method to oxygen, uncertainty in the absolute values does not affect the correction in this case.

§ 2. *Anhydrous Ferrous Sulphate.* With ferrous sulphate practically anhydrous we found that the susceptibility at higher temperatures increased, and at lower temperatures decreased as the temperature was diminished. Much to our regret we were compelled for the same reasons as before to postpone for some time a continuation of these experiments. In particular we should have liked to have carried out experiments in a bath of liquid nitrogen to settle definitely at what temperature occurs the maximum susceptibility which is clearly indicated by our other results. This is evident from Table III in which we collect our data. The measurements at 143°.1 K and 170°.6 K were made in a bath of liquid ethylene.

TABLE III.

Practically anhydrous ferrous sulphate.

T	$\chi.10^6$
293° K	65.0
170.6	102.6
143.1	117.5
20.3	251
18.0	240
15.9	231
13.9	221

Indeed, these results show without doubt that cases of maximum susceptibility can and do occur. We communicated this result to the Swiss Physical Congress in August, and at the same meeting Debye gave an explanation of this maximum which was based on the theory of finite elements of action This supports the hypothesis communicated last May to which we had been led by our experimental results, that deviations from Curie's law are intimately related to the energy properties of the Planck vibrators.

§ 3. *Conclusions.* If we supplement the reasoning developed in § 3 of Communication N⁰. 122*a* by the present results for oxygen and anhydrous ferrous sulphate, we are led to conclusion that for a class of paramagnetic substances there exists a region of higher temperatures within which deviations from Curie's law are but insignificant, while as the temperature sinks deviations slowly increase so much that a maximum is eventually reached, and then, with further lowering of the temperature, the susceptibility, instead of increasing begins to decrease, disappearing finally at the absolute zero of temperature. This generalisation renders probable the assumption that, with respect to paramagnetism, there exist corresponding (absolute) temperatures (temperatures at which deviations from Curie's law are the same) which, for every substance, must be considered proportional to a certain (absolute) temperature characteristic of the particular substance, the *temperature of the maximum specific susceptibility* of the substance. This temperature, then, would be very low for crystallized gadolinium sulphate, for oxygen it would lie not far below the boiling point of hydrogen, and for anhydrous ferrous sulphate it would lie well above the latter temperature. Were this generalisation confirmed for definite classes of substances, it would lead to a general law of which advantage could be taken in the evaluation of the number of magnetons in the molecules of solid substances belonging to those classes.

COMMUNICATIONS

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H. KAMERLINGH ONNES.
Director of the Laboratory.

N°. 124b.

H. KAMERLINGH ONNES. — "Further Experiments with Liquid Helium. F. Isotherms of Monatomic Gases etc. IX, Thermal Properties of Helium." (*With a plate*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **30 December 1911**, p. 793—799.

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES. — "*Further Experiments with Liquid Helium. F. Isotherms of Monatomic Gases etc.* IX. *Thermal Properties of Helium*".

(Communicated in the meeting of November 25, 1911).

§ 1. *Vapour pressures of helium above the boiling point. Critical pressure and critical temperature for helium.* The helium-cryostat described in Comm. N⁰. 123 (June 1911) made it possible for me to undertake an experimental determination of the critical constants for helium. A determination of these constants was particularly desirable with a view to investigating the deviation of helium from the law of corresponding states. With that end in view I had endeavoured as far back as 1909 (see Comm. N⁰. 112, June 1909) to measure the critical pressure to at least a first approximation; I then obtained from expansion experiments the value $p_k = 2.75$ atm. while in 1908 I had estimated that p_k should not be much greater than 2.3 atm. and that T_k should be 5° K.

From the experiments described in the present paper it will be clearly seen that these expansion experiments led to too large a value; but it must be remembered that in communicating those results (Comm. N⁰. 112, 1909) it was definitely stated that the measurements made could only be regarded as a preliminary approximation. Those experiments were made under variable temperature, while it is very desirable for determinations of critical constants that one should have available a cryostat giving a range of constant temperatures in the neigbourhood of the critical temperature. Moreover, there was no stirrer inside the tube in which the helium was brought to its critical state. During the experiments the temperature within the experimental tube seems to have been so different at different levels, that the impression of the presence of a meniscus could have been obtained while the pressure was higher than that which we now find to be the critical. Besides, on expansion to 2.5 atm. this would have occasioned the appearance of a local mist such as is ordinarily seen in the critical state. It must be left for further experiment to clear up the exact circumstances obtaining during those expansion experiments, and to explain why they are apparently able to afford only an upper limit to the value of the critical pressure. Under the much more favourable circumstances of temperature constancy and effective stirring under which the present experiments were conducted, vapour pressures could be measured close up to the critical point, and in conjunction with them the critical pressure could be obtained. For this constant, the value 2,26 atm. was obtained, which must, from the nature of the method adopted, be regarded as a lower limit. We must regard it as fortuitous that this value differs so slightly from the estimate of 1908.

In the present experiments the critical temperature was determined directly for the first time. I found $T_k = 5^\circ$ K. In 1908 T_k was estimated as slightly in excess of 5° K. With regard to the value $T_k = 5.^\circ 8$ K which was deduced in Comm. N⁰. 119 (Febr. 1911) from vapour pressures below the boiling point, using the experimental value of p_k of 1909 (Comm. N⁰. 112), it was even then suspected that the value would prove too high, so that in § 5 of the same communication the value $T_k = 5.^\circ 5$ K was taken. (The reason for its excessive value is now seen to be that the value of p_k used for the deduction was too high.)

The present experiments were carried out in the following manner. (See accompanying Plate fig. 1.) In the helium glass S_7 of the helium cryostat described in Comm. N⁰. 123 (June 1911, parts of the apparatus are represented on the accompanying Plate by the letters which were used for the same parts in the diagram given with that Communication) is placed another glass reservoir of which the lower part consists of a double walled vacuum glass a_1 provided with an outlet spiral a_0; the upper part a_2 is single-walled, and terminates in two narrow tubes, a_3 and a_4. One of these tubes, a_4, is, at its upper extremity, provided with a side tube which is closed by a tap. The ends of both a_3 and a_4 are cemented to the tubes b_3 and b_4 (b_{40}, b_{41}), whose functions will presently be described, so that the reservoir a is completely closed from above. If liquid helium is present in the helium glass S_7, by opening the valve a_5 it can be forced through a_0 into the inner chamber which is itself protected by the vacuum vessel a_1. It the tap a_5 is now closed, ordinary communication of heat by conduction and radiation, supplemented, if necessary, by development of JOULE heat in the small coil of constantin wire d, will drive the liquid back along a_0 leaving the inner chamber filled with helium vapour. The lower portion of this chamber thus becomes a cryostat chamber, protected by a transparent vacuum glass and immersed in liquid helium, an inner cryostat whose *temperature* can be brought to *a little above that of the surrounding liquid helium* in the outer cryostat. In this *cryostat for temperatures just above the boiling point of helium* is now placed the experimental reservoir b_1 which serves for the determination of the critical constants of helium. This reservoir is concave underneath, b_2; it is also provided with two narrow tubes one of which b_{30} contains the thermometer capillary, being fused to it at b_{31}, while the other b_{40} admits the stirrer string, and at the same time allows helium to be admitted or removed through b_{42} or, if necessary, to be blown off through b_{43}.

The temperature is maintained constant and uniform by means of the stirrer b_5 which is operated by the string b_7 through the action of an electromagnet upon the soft iron cylinder b_8.

The temperature of the helium inside b was measured by a helium thermometer whose reservoir θ_1 was placed within the experimental reservoir b. In a note at the end of this section we shall return to this thermometer, which is, for the rest, the same in principle as that described in Communication N^0. 119 (see accompanying Plate fig. 3). The thermometer capillary goes by b_3 and then a_4 to the outside.

To fill the experimental reservoir b with liquid helium, pure compressed helium is admitted along b_{42} through the tap h (fig. 2). while the inner cryostat is kept full of liquid helium by drawing off through a_5 the vapour that is formed. Part of the tube which supplies pure helium to the reservoir b consists of a spiral immersed in liquid air, through which the gas must first pass. The necessary connection with the mercury vacuum pump can be obtained through the tap f (fig. 2). The pressure of the gas in the supply tube is read on the spring manometer g, and the pressure of the helium in the experimental reservoir is read on the open mercurry manometer M (Fig. 2).

At temperatures a little above the boiling point a constant temperature is obtained within the experimental reservoir by leaving the valve k a little open, so that a small amount of gas flows off uniformly through it. By the resulting vaporization the liquid in b is cooled, and the rate at which the gas escapes is so regulated that while stirring is kept up the temperature remains constant. The pressure difference due to the escape of the gas is neglected. On stirring, the liquid forms an emulsion as if of oily liquid drops. In the neighbourhood of the critical temperature this emulsion of liquid in vapour assumes the appearance of a milky cloud. During the measurements, the stirrer was repeatedly stopped for a moment so as to see at what level in the reservoir the meniscus of the non-emulsified liquid stood.

In this way determinations of vapour pressures were made with perfect regularity up to 5°.15 K. but from that point onwards it was found difficult to complete a temperature measurement in the short time elapsing before the liquid meniscus reached the bottom of the resevoir on account of the rapid escape of vapour. On that account the tap was then closed and the temperature was regulated by passing a current through the warming coil d and at the same time allowing gas to escape through a_5, so that the experimental reservoir was cooled by the passing over its walls of the colder vapours arising from the helium vaporising within the inner cryostat. In this way measurements were made of vapour pressures to a point very close to the critical temperature. Just a little higher than the highest temperature thus attained, but higher by an amount which could not be measured, there was still a slight trace of milky cloud to be seen following the motion of the stirrer, while at a temperature just a little higher still, but with a temperature difference no more measurable than before, the experimental tube remained quite clear. The indications of the pressure were much more sensitive than those of the temperature. I could tell accurately to within a centimetre the pressure of transition of the one state to the other within the reservoir. The temperature change corresponding to this small change of pressure is still a good deal smaller than that which has just been mentioned as too small for measurement. The pressure at which the transition was observed was taken to be the critical pressure. As we have already mentioned, the manner in which this value has been obtained makes us regard it as a lower limit; but still, the actual value can only be very slightly greater. We may therefore assume $T_k = 5^\circ.25$ K, $p_k = 2.26$ atm. (see Table).

The thermometric measurements with the constant volume[1] helium thermometer, for which, as well as for other assistance, I gladly acknowledge my indebtedness to Dr. C. DORSMAN, were made with a zero pressure of 300 mm. This is about double the zero pressure used in the determinations of Comm. N⁰. 119. For other measurements the zero pressure was 667 mm. and for the measurements made in 1908 it was practically 15 atm.

From the agreement between the values of the boiling point of helium obtained under various conditions I think I may safely put the boiling point at 4°.26 K, or better in round numbers 4°.25 K, with an accuracy greater than 0°.1. The same degree of accuracy can be ascribed to the value found for the critical temperature of helium.

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[1] Plate I, fig. 3 shows the helium thermometer modified for very low temperatures. The figure should be compared with fig. 1 of Pl. I. Comm. N⁰. 119; in the two figures identical parts are indicated by the same letters, while those parts which have undergone modification are indicated in the new figure by accented letters. To avoid development of vapours at cemented joints and to avoid metal capillaries at places where a constant high vacuum is necessary for control experiments, the steel blocks f' and $f'a$ with their reading points have been brought inside the glass tubes and fastened to the walls with a minimum of sealing wax. To reduce the dead space, e' has been rounded off above. The connections of the adjusting tubes with the reservoir d_5 and with the thermometer capillary as far as the tap $K\theta_0$ are now made completely of glass d_2', d_3' with a ground joint at d_4'. The connections at $g'_0\, la'_0\, l_0'\, l_3'\, la'_3$ are also all ground joints (when these joints were being greased, care was taken that the grease did not come in contact with the mercury). $K'\theta g$ has been introduced for the filling of the thermometer for which the ground joint $K\theta_{g_2}$ is also used, l_2' has been taken of such a size that in filling the thermometer the mercury from g_1' can be brought over into l'_2 An internal air-trap is introduced at d_{51}. The copper thermometer capillary Th'_2 is joined to the capillary d'_{01} by the coupling piece d'_{02} and the capillary d'_{01} is in turn cemented on with the sleeve d'_{00} above the tap $K\theta_0$.

A correction of —0.°07 has to be applied to the figures given in col. II of the Table in § 4 of Comm. N°. 119 on account of an index-correction ascribed to development of vapour and for this reason not introduced into the calculation made at that time. The supposed development of vapour has since been ascertained to be due to a small leak and the correction has therefore to be applied.

The thermometry of these low temperatures, hower, must still be made the subject of a special investigation. In particular, an investigation must be made of the correction which is to be applied on account of the influence which, as appears from KNUDSEN's researches, the mean free path of the gas molecules in the upper part of the thermometer capillary can exert upon the value of the pressure. It might, for instance, be, that the mean free path could no longer be neglected in comparison with the width of the capillary.

Expressing p in atmospheres, the following results were obtained:

TABLE I.

Vapour pressures of helium	
T	$760\ p_{\text{coëx}}$
4°.28 K	767
4.97	1329
5.10	1520
5.15	1569
5.22	1668
5.25 critical	1718 critical

§ 2. *Values of certain thermal constants of helium.*

In Comm. N⁰. 119 a value for the constant f_W in the VAN DER WAALS vapour pressure formula (with common logarithms) was found which was strikingly low, viz. 1.2. This value was obtained from the slope at the boiling point of the tangent to the curve giving log p as a function of $\frac{1}{T}$, and from the value which was then assumed for the critical pressure, viz. 2.75 atm.

If we use the value of p_k now given, we find from the tangent to the curve at the boiling point the value $f_w = 1.3$ for common logarithms, so there is still a large deviation from the ordinary value of f_w. But the figures which we now give have brought to light the important property that *above the boiling point* f_w *increases very rapidly.* If the tangent is drawn at the critical point the common logarithm constant is found to be $f_{wk} = 1.95$ (round numbers from 1.94). This value of f_{wk} is still smaller than that for any other substance, but still, considering the gradual transformation of the equation of state as one goes from substances of high to substances of low critical temperature, it agrees pretty well with that for other substances (lowest 2.2).

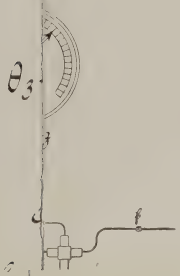
To be able to compare f_{wk} with the value deduced from the critical constants we want to get v_k. v_k is now the only one of the critical constants which has not yet been determined from direct observation; it may, however, be assumed in the meantime that it can be deduced with sufficient accuracy from the observed densities of co-existing liquid and saturated vapour by the method adopted in Comm. N⁰. 119. This method gives $\rho_{kd} = 0.066$ and $v_{kd} = 0.00271$.

In contradiction to what I have before deduced, our new knowledge of f_{wk} and the improved data for p_k, v_k and T_k confirm, at least approximately, VAN DER WAALS's expectation that the relation he deduced between the critical constants would be found to hold for helium also.

The critical virial quotient $\dfrac{RT_k}{p_k v_k} = K_4$ now becomes 3.13 (for argon it is 3.283, see Comm. N⁰. 120); hence using VAN DER WAALS's relation $K_4^2 = \dfrac{64}{27}(K_6 - 1)$ we get a value 5.13 for the critical vapour pressure coefficient $\left(\dfrac{T}{p}\,\dfrac{dp_{\text{coëx.}}}{dT}\right)_k = K_6$; this leads to the common logarithm constant $f_{wk} = 2{,}2$, whereas 1,95 is the value actually found. The difference remaining is not great, and, in connection with it, it must be remembered that the value now found for p_k is a lower limit, and that the relation would hold better for a higher value of p_k. We may therefore conclude that the apparent association at the critical temperature is, in the case of helium, still subject to practically the same laws as hold for ordinary normal substances.

The great difference between helium and normal substances makes itself apparent at lower reduced temperatures, as shown by the marked diminution in the value of f_W at lower reduced temperatures at which also the liquid density attains a maximum. This difference can well be the result of an influence of proximity to the absolute zero at very low temperatures quite different from that which obtains ordinarily for the same values of the reduced temperature, due to the fact that the liquid state lies much closer to the absolute zero with helium them with any other substance.

H. KAMI of Monatomic Gase



H. KAMERLING ONNES. "Further Experiments with Liquid Helium. F. Isotherms of Monatomic Gases etc. IX. Thermal Properties of Helium."

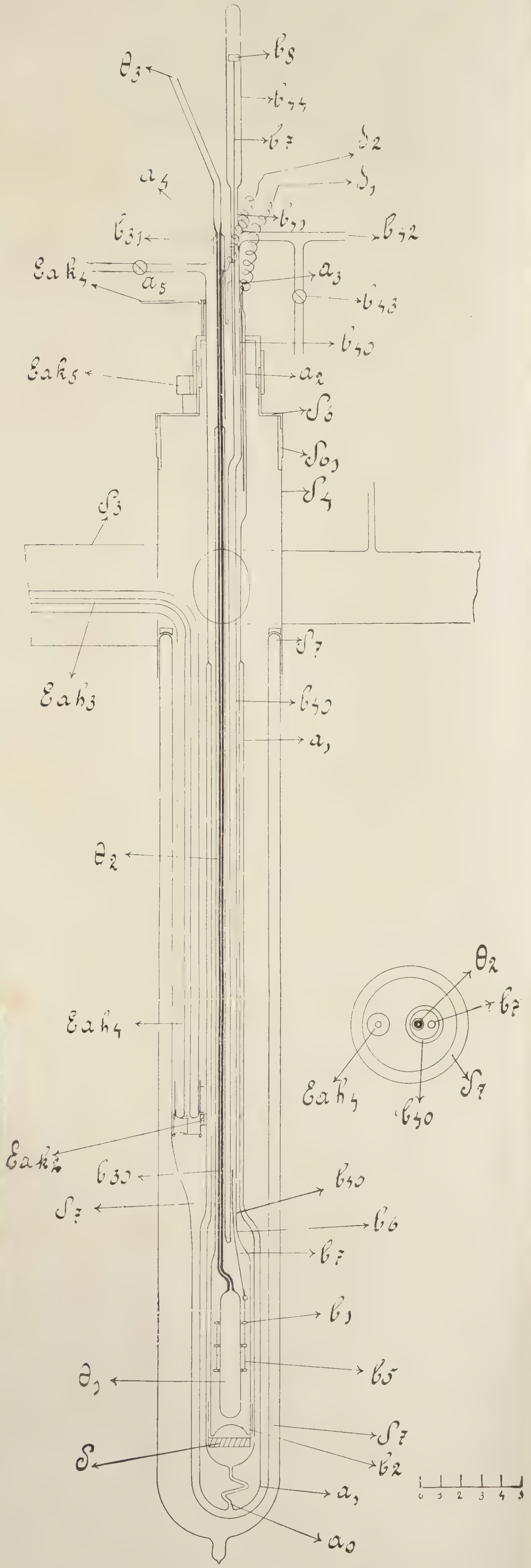


Fig. 1.

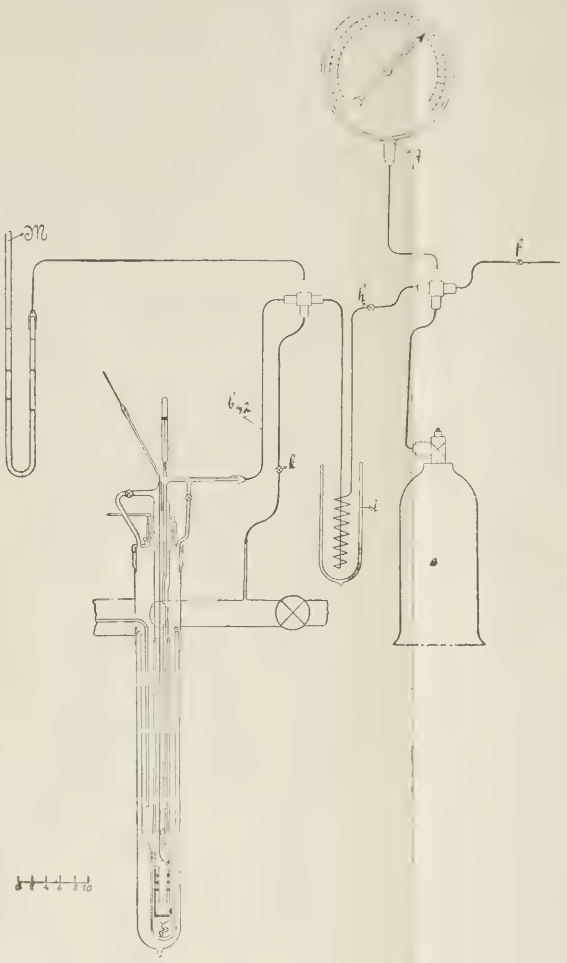


Fig. 2.

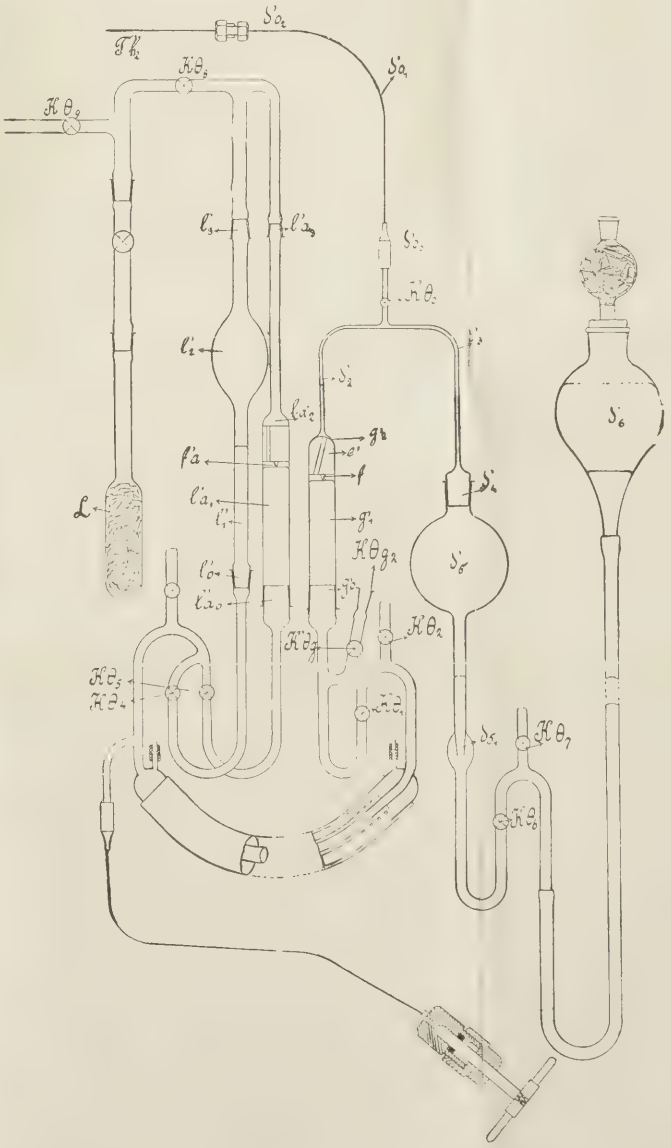


Fig. 3.

Communication No. 124b.

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Director of the Laboratory.

N°. 124c.

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H. KAMERLINGH ONNES. — "Further Experiments with Liquid Helium. G. On the Electrical Resistance of Pure Metals, etc. VI On the Sudden Change in the Rate at which the Resistance of Mercury Dissappears." (*With a plate.*)

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **30 December 1911**, p. 799—802.

Eduard IJdo — Printer — Leiden.

H. KAMERLINGH ONNES. — "*Further Experiments with Liquid Helium.* G. *On the Electrical Resistance of Pure Metals, etc.* VI. *On the Sudden Change in the Rate at which the Resistance of Mercury Disappears.*"

(Communicated in the meeting of November 25, 1911).

§ 1. *Introduction.* In Comm. N⁰. 122*b* (May 1911) I mentioned that just before this resistance disappeared practically altogether, its rate of diminution with falling temperature became much greater than that given by the formula of Comm. N⁰. 119. In the present paper a closer investigation is made of this phenomenon.

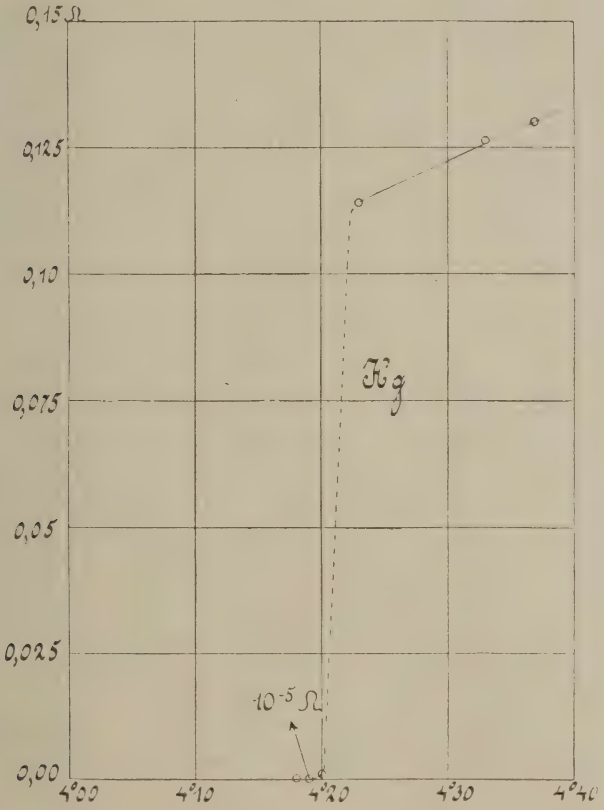
§ 2. *Arrangement of the resistance.* A description was given in Comm. N⁰. 123 (June 1911) of the cryostat which, by allowing the contained liquid to be stirred, enabled me to keep resistances at uniform well-defined temperatures; and in that paper I also mentioned that measurements of the resistance of mercury at the lowest possible temperatures had been repeated using a mercury resistance with mercury leads. The immersion of a resistance with such leads in a bath of liquid helium was rendered possible only by the successful construction of that cryostat.

The accompanying Plate, which should be compared with the Plate of Comm. N⁰. 123, shows the mercury resistance with a portion of the leads; it is represented diagrammatically in fig. 1. Seven glass *U*-tubes of about 0.005 sq. mm. cross section are joined together at their upper ends by inverted *Y*-pieces which are sealed off above, and are not quite filled with mercury; this gives the mercury an opportunity to contract or expand on freezing or liquefying without breaking the glass and without breaking the continuity of the mercury thread formed in the seven *U*-tubes. To the *Y*-pieces b_0 and b_8 are attached two leading tubes Hg_1, Hg_2 and Hg_3, Hg_4 (whose lower portions are shown at Hg_{10},

Hg_{20}, Hg_{30}, Hg_{40}) filled with mercury which, on solidification, forms four leads of solid mercury. To the connector b_4 is attached a single tube Hg_5, whose lower part is shown at Hg_{50}. At b_0 and b_8 current enters and leaves through the tubes Hg_1 and Hg_4; the tubes Hg_2 and Hg_3 can be used for the same purpose or also for determining the potential difference between the ends of the mercury thread. The mercury filled tube Hg_5 can be used for measuring the potential at the point b_4. To take up less space in the cryostat and to find room alongside the stirring pump Sb, the tubes which are shown in one plane in fig. 1 were closed together in the manner shown in fig. 2. The position in the cryostat is to be seen from fig. 4 where the other parts are indicated by the same letters as were used in the Plate of Comm. N⁰. 123. The leads project above the cover Sb_1 in a manner shown in perspective in fig. 3. They too are provided with expansion spaces, while in the bent side pieces are fused platinum wires Hg_1', Hg_2', Hg_3', Hg_4', Hg_5' which are connected to the measuring apparatus. The apparatus was filled with mercury distilled over in vacuo at a temperature of 60° to 70° C. while the cold portion of the distilling apparatus was immersed in liquid air.

§ 3. *Results of the Measurements.* The junctions of the platinum wires with the copper leads of the measuring apparatus were protected as effectively as possible from temperature variation. The mercury resistance itself with the mercury leads which served for the measurement of the fall of potential seemed, however, on immersion in liquid helium to be the seat of a considerable thermoelectric force in spite of the care taken to fill it with perfectly pure mercury. The magnitude of this thermo-electric effect did not change much when the resistance was immersed in liquid hydrogen or in liquid air instead of in liquid helium, and we may therefore conclude that it is intimately connected with phenomena which occur in the neighbourhood of the transition of solid to liquid mercury. A closer investigation of the true state of affairs was postponed for the meantime, and the thermoelectric force was directly annulled during the measurements by an opposed electromotive force taken from an auxiliary circuit. The magnitude of this thermoelectric force, which for one pair of the leads came to about half a millivolt, made it impracticable to reverse the auxiliary current as is usually done in the compensation method. The resistance of the mercury thread was then obtained from the differences between the deflections of the galvanometer placed in circuit with Hg_2 and Hg_3 and the compensating electromotive force, when the main current passing through the resistance was reversed. The galvanometer was calibrated for this purpose.

In the accompanying figure is given a graphical representation of the resistances observed [1]).



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[1]) For the resistance of the solid mercury at 0° C. extrapolated from the melting point nearly 60 Ohm can be accepted. In the solidifying process differences occur which make necessary special measurements to be able to give the exact proportion of the resistance of the wire at

As a former experiment showed that there was a pretty rapid diminution of the resistance just below the boiling point of helium, there arose in the first place a question as to whether there exists between the melting point of hydrogen and the boiling point of helium a point of inflection in the curve which represents the resistance as a function of the temperature. The temperature of the bath was therefore raised above the boiling point by allowing the pressure under which the liquid evaporated to increase, an operation possible with this cryostat by closing the tap Eak_2, leading to the liquefier. The excess pressure was read on an oil manometer connected to S_3. These measurements showed that from the melting point of hydrogen to the neighbourhood of the boiling point of helium the curve exhibited the ordinary gradual lessening of the rate of diminution of resistance, practically the same as given by the formula of Comm. N⁰. 119. A little above and a little below the boiling point, from 4°.29 K. to 4°.21 K. the same gradual change was clearly evident (cf. the fig.), but between 4°.21 K. and 4°.19 K. the resistance diminished very rapidly and disappeared at 4°.19 K. (Temperature measurements are here given with 4°.25 K. as the boiling point of helium).

During the discussion initiated by the communication of these results to the Brussels "Conseil SOLVAY" (2 Nov. 1911) M. LANGEVIN asked if other properties of the substance displayed similar sudden changes, as would be the case if mercury underwent a structural modification at 4°.20 K. Experiments with the object of settling this point were, of course, immediately planned when this phenomenon was observed, but they have not yet been concluded. It can well be, however, that, should there exist such a new modification, it would differ from ordinary mercury at higher temperatures chiefly by the property that the frequency of the vibrators in the new state has become greater, and therefore the conductivity rises to the extremely large value exhibited below 4°.19 K.

§ 4. *The motion of electricity through mercury at temperatures*

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helium temperatures to that at 0° C. (solid extrapolated from the melting point). Therefore here are given the resistances themselves. [Note added in the translation.]

below 4°.19 K. The next step was as in the earlier experiments to try by sending a comparatively strong current through the resistance, to obtain an upper limit to the value which must be ascribed to the resistance when this has practically vanished as is the case at 3°.5 K. The peculiarities of the phenomena which then occur make it desirable to experiment first with a modified apparatus before proceeding further.

H. KAMERLINGH ONNES. „Further Experiments with Liquid Helium. G. On the Electrical Resistance of Pure Metals etc. VI. On the sudden change in the Rate at which the Resistance of Mercury Disappears.”

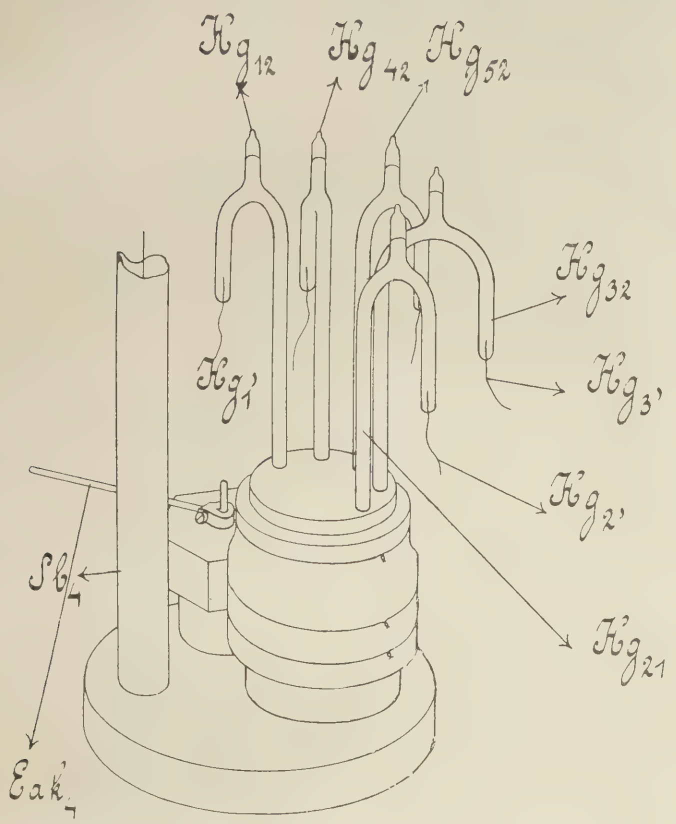
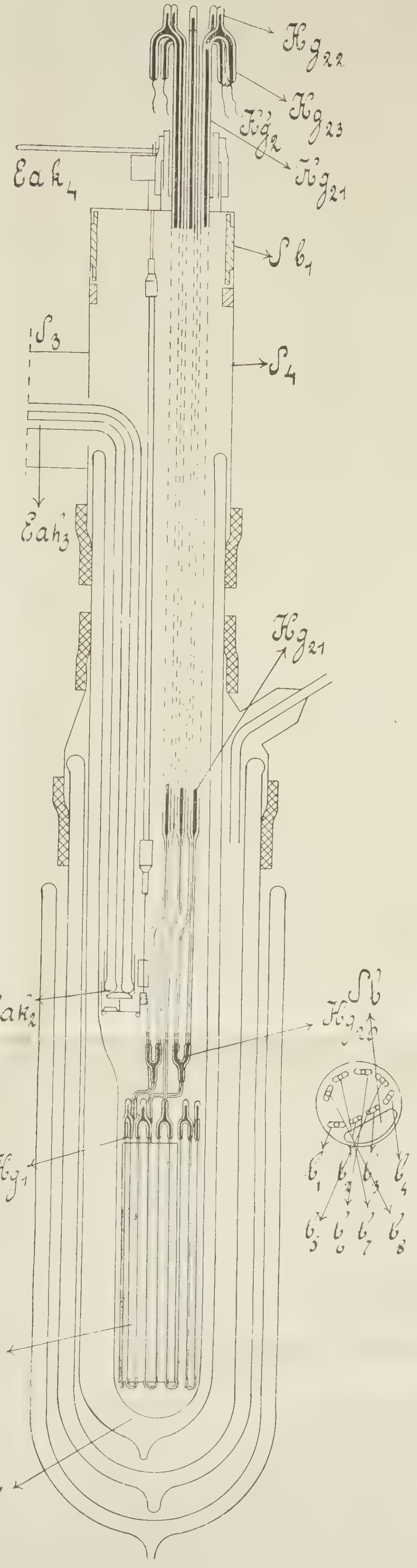


Fig. 3.



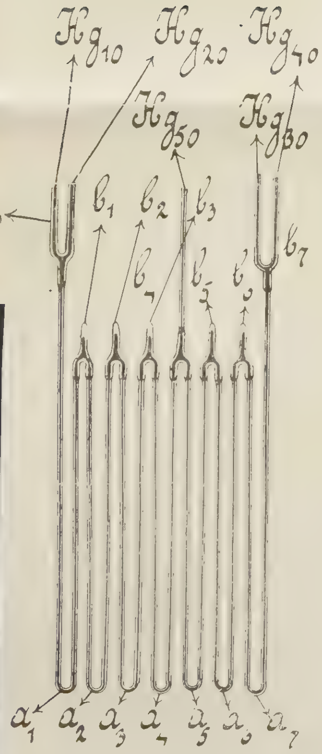


Fig. 1.

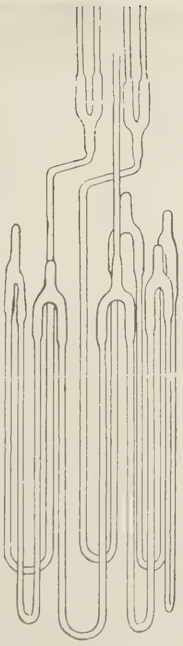


Fig. 2.

Fig. 4.

Communication No. 124c.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

[illegible] UNIVERSITY OF [illegible]

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 125.

J. P. KUENEN. "Investigations concerning the miscibility of liquids".

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **30 December 1911**, p. 725—730.)

EDUARD IJDO — PRINTER — LEIDEN.

J. P. KUENEN. — "*Investigations concerning the miscibility of liquids*".

Several years ago I began a systematic experimental investigation of the miscibility of liquids, in particular as regards the influence of temperature and pressure, or to express it differently an investigation into the shape and the change of shape of the projected liquid plait of the ψ surface and its position relatively to the vapour-liquid plait.

A fertile combination and one which turned out interesting in many respects was found in the saturated hydrocarbons with the lower alcohols. The investigations of these and other mixtures which was discontinued from various causes was recently taken up again and I propose to communicate the results to the Society from time to time.

A decided gap in the research was the absence in the series of hydrocarbons of a term with four carbon atoms and in one of my last papers on the subject ¹) I stated, that the preparation of normal butane had been tried and that it had not met with the desired success. The method was by electrolysis of sodium propionate, which yields a very impure gas, the chief products being carbon dioxide and ethylene. The treatment with bromine for the absorption of ethylene showed that bromine acts on butane and a repeated attempt to procure pure butane by this method did not succeed.

Better methods were not then available. In the mean time two new methods of preparing hydrocarbons from bromides or iodides have been published: one by the action of sodium dissolved in liquid ammonia (LEBEAU) and the other (GRIGNARD) with magnesium. Butane has been prepared by the first method by LEBEAU himself ²) and by the second method by OUÉDINOFF ³).

The results obtained by them do not agree accurately. I have applied both methods and again obtained results which do not quite

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¹) J. P. KUENEN. Phil. Mag. (6) 6 p. 647. 1903.

²) P. LEBEAU. Bull. Ac. R. de Belg. 1908 p. 300—304.

³) OUÉDINOFF. Bull. Soc. Chim. de Belg. (23) Juin 1909.

agree either with each other or with those of the other investigators. I subjoin a table of the critical constants and boiling points.

Normal Butane

Observer	Method of preparation	Crit. Temp.	Crit. press.	Boiling point
Lebeau	Lebeau	151—152		0.5
Ouédinoff	Grignard	146.5		0.6
Kuenen	Electrolysis	158.5		
"	"	145.5		— 1.7
(*a*) "	Lebeau	148.7	± 39	
(*b*) "	Grignard	150.8	37.5	— 0.1

The experiments communicated below were made with the two samples of butane indicated as (*a*) and (*b*) [1].

In the mean time some observations have been made by Timmermans and Kohnstamm [2] on mixtures of butane with a few other substances, butane having been given to hem by Ouédinoff.

I begin by communicating a few critical endpoints [3] which I have determined.

Critical endpoints

methylalcohol	+ isopentane	10.5
"	+ *n.* pentane	19.4 [4]
"	+ *n.* butane (*b*)	17.0 (T. and K. 16.6 [5])
aethylalcohol	+ isopentane	—30
"	+ *n.* butane (*a*)	+ 37.5.

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[1] Later on I hope to communicate a set of physical constants of butane obtained with sample (*b*), mainly determined by S. H. Visser, science student at Leiden.

[2] J. Timmermans and Ph. Kohnstamm. Proc. XII 1909—10, p. 234; table on page 239.

[3] By critical end-point is meant the critical point of the liquid layers in the presence of vapour, i.e. the point where the liquid plait touches the vapour-liquid plait. In former papers I have usually called this point the critical mixing-point.

[4] Determined by me on a previous occasion (l. c. p. 647) and erroneously attributed by Timmermans and Kohnstamm (l. c.) to isopentane instead of normal pentane.

[5] l. c. p. 239.

The critical end-point for methylalcohol and normal butane agrees well with the result of the other observers.

Very unexpectedly an entirely different result was obtained when use was made of butane (*a*), although in its constants but little differing from butane (*b*). This difference must be due to some impurity and although I cannot throw any light on the nature or action of this impurity, I will describe the observations, as they have brought to light a new phenomenon which appears to be of interest.

When a mixture of butane (*a*) and methylalcohol was heated in a compression tube (CAILLETET) in the presence of the vapour, the surface between the liquid layers disappeared about 22°, a somewhat higher temperature than for a mixture of butane (*b*) (17°.0). When however the temperature was further raised the meniscus soon reappeared and the definite critical end-point was not reached till 38°. Beyond 38° no separation of two liquids took place. The application of pressure revealed a similar abnormality: at temperatures above 22° a gradual increase of the pressure always had the effect of making the meniscus grow faint and disappear and afterwards permanently reappear.

It is not difficult to see what shape has to be attributed to the liquid plait in the v-x-diagram in order to represent the above phenomena. The fact that pressure ultimately produces separation of the two liquids shows that the plait is open towards the x-axis. This is in accordance with the result obtained by TIMMERMANS [1]), that the critical temperature of the liquids is in this case raised by pressure, which means that beyond the critical end-point the liquid plait lies outside the vapour-liquid plait with its plaitpoint turned towards the latter. But the abnormal phenomenon was not noticed by him, nor have I been able to reproduce it with mixtures of butane (*b*).

If the liquid surface temporarily disappears as described, the plait would have to consist of two parts as shown in fig. 1 where the relative position with respect to the liquid branch of the vapour-liquid plait is also indicated. It seems unnecessary to show in detail, that the behaviour of the mixture under changes of pres-

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[1]) J. TIMMERMANS. Thèse Bruxelles 1911, p. 82.

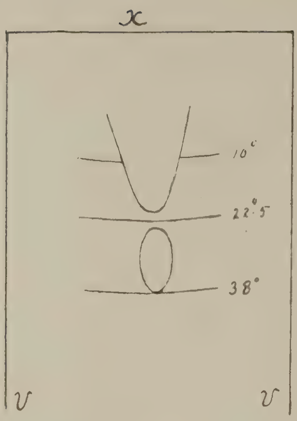

Fig. 1.

sure or temperature agrees with the assumed diagram. In itself a diagram of this nature is by no means improbable. In this connection it is important to consider the behaviour of a mixture of methylalcohol with isobutane as observed by TIMMERMANS. The critical end-point is in that case very near a point where the liquid plait divides and it would be quite possible for the plait in the case of the nearly allied normal butane to be divided in the manner assumed in fig. 1.

Further investigation of the phenomenon showed however that the assumption was incorrect. It may be remarked that the observations were extremely difficult owing to the great indistinctness of the liquid surface compared to other mixtures (TIMMERMANS notes the same peculiarity for mixtures of methylalcohol and isobutane). When I repeated the observations under the most favourable conditions with regard to illumination I found that the meniscus did not really disappear when it seemed to do so temporarily before, but as a rule remained just visible in the form of a dark and sometimes slightly coloured horizontal line near the axis of the tube.

The moment of minimum distinctness could be observed with fair accuracy; in the table are given the observed pressures as also some three-phase pressures. The readings were not more accurate than to about $^1/_2$ atmosphere.

Temp.	Least distinctness at	Three phase pressure
14.0	— atm.	$1^1/_2$ atm.
22.5	2	2
22.8	$3^1/_2$	—
24.2	$9^1/_2$	$2^1/_4$
25.0	$13^1/_2$	—
25.5	16	—
26 3	$21^1/_2$	$2^1/_2$
27.2	$25^1/_2$	—

Temp.	Least distinctness at	Three phase pressure
28.5	33 atm.	— atm.
29.3	36½	—
31.0	43	—
32.4	53½	3
33.7	62½	3½
36.8	75	—
37.0	78	—
38.1	—	4¼
38.2	—	Cr. end-point
38.6	84	—

The plait cannot therefore be divided as in fig. 1 and our supposition has to be modified in the sense that the plait is only strongly contracted as in fig. 2.

But the facts speak against this supposition too; for with fig. 2 one would expect phenomena which also occur near a critical point e.g. a distinct change in the relative volumes of the two phases (at 38° this phenomenon was very marked) and a slow settling down of the liquids after having been stirred up. This was not what happened at the points of indistinctness: in so far as the meniscus was visible at all, it reappeared (after stirring) comparatively quickly showing that there was a difference in density between the liquids of the same order as at other points of the plait.

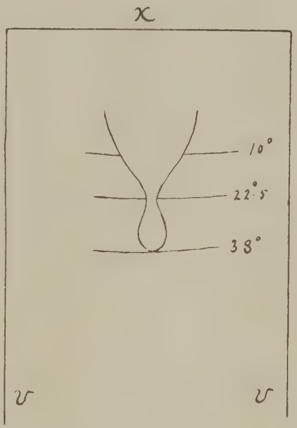

Fig. 2.

The only explanation which remains is that the refractive indices of the liquids become equal: the plait need not have any abnormal shape, but at some distance from the plaitpoint there is a point where the two coexisting liquids have the same index, which point, if outside the vapour liquid plait i.e. above 22°, may be reached by change of pressure. Though this phenomenon cannot but be very rare, it is not by any means impossible even with two pure substances. When the indices of the components differ little, there is a chance that the phenomenon may occur: there will be a maximum or minimum in the indices in that case for one particular proportion. Probably the index of butane is not much higher than that of methylalcohol (this question is being investigated): the indistinctness of the surface between the liquids even at a distance from the critical region makes this problabe.

The question remains what impurity may have occasioned the difference in the behaviour of the two samples of butane in this respect[1]). I am inclined to think, that butane (*b*) was purer than butane (*a*), especially as the experiments were made with the last remaining fraction of the butane (*a*) available, in which an admixture of higher boiling point may have been concentrated and during the operation of introducing the substances into the compression tube some moisture may also have got into the tube. However that may be it is very remarkable that an impurity which cannot have been large, as appears from the constants of the substance, can have had such a strong effect on the mixing phenomena, shifted the critical end point from 17° to 38° and moreover produced the abnormality in the refractive index.

Finally it may be remarked, that the probable conclusion with respect to the impurity of the butane (*a*), raises some doubt as to the accuracy of the critical end-point for mixtures of ethylalcohol and butane. I hope shortly to be able to throw more light on the questions raised by these observations.

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[1]) If the mixture contains a third substance it is properly speaking no longer possible to represent the phenomena with the aid of a v-x-diagram, unless the admixture is so slight that it may be disregarded for the purpose of the graphical representation.

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

* * *

N°. 126.

* * *

ALBERT PERRIER and **H. KAMERLINGH ONNES**. — Magnetic researches. V. The inital susceptibility of nickel at very low temperatures.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **24 Februari 1912**, p. 1138—1141.

Eduard IJdo — Printer — Leiden.

ALBERT PERRIER and **H. KAMERLINGH ONNES.** *Magnetic Researches. V. The initial susceptibility of nickel at very low temperatures.*

§ 1. *Introduction.* To establish the general law for the effect of temperature upon magnetic phenomena is a much more complicated problem in the case of ferromagnetic substances than in the case of substances whose susceptibility isindependent of the field; for, with ferromagnetic substances — just as when an investigation is being made of the influence of change of field upon susceptibility at constant temperature — a distinction has at once to be drawn between three entirely distinct cases. The region of *weak* fields is identified by a practically total absence of hysteresis; in the region of *moderate* fields the susceptibility changes very rapidly and hysteresis plays an all-important part; while in the region of *strong* fields or of *saturation* magnetisation changes but very little more with change of field. The intricacy of the general problem embodying these successive cases as well as various further peculiarities such as the irreversibilities depending on temperature and on time arises from the very nature of ferromagnetism itself. In these circumstances, therefore, an experimental investigation as well as a theoretical treatment of the whole problem of the change of ferromagnetism with temperature can hardly be otherwise made than by a systematic subdivision of the investigation into various sections each of which can be treated separately. The natural method of treating the problem seems to be to ascertain the temperature functions which hold good throughout each of the regions, and in that case the two extreme regions are obviously the easiest to investigate, for then at least one of the phenomena, hysteresis, is no longer of any account.

The investigation of one of these extreme regions, that of saturation, has already been pretty well completed, not only at high but also at very low [1]) temperatures. The results then obtained were used by WEISS [1]) in the research which led him to the important discovery of the magneton. In his recent dissertation RADOVANOVITCH [2]) has worked in the other extreme region, that of initial susceptibility (i. e. susceptibility in weak fields) but only at temperatures above 0° C. His work, done exclusively with nickel, led principally to the following result.

---

[1]) P. Weiss and H. Kamerlingh Onnes, Comm. N°. 114 (Febr. 1910).

If $\mathcal{I}$ is the magnetisation induced by a field of strength H, then, for fields below about 0.5 gauss, and at constant temperature [3]),

$$\mathcal{I} = aH + bH^2,$$

or

$$K = a + bH.$$

RADOVANOVITCH has now found that between 17° C. and the CURIE point, a and b are given for nickel as functions of the temperature by

$$a = A \sqrt[4]{\left(\frac{I_0}{I} - 1\right)}$$

$$b = B\left(\frac{I_0}{I} - 1\right).$$

I and I_0 are the saturation magnetisations at the experimental temperature and at the absolute zero respectively, A and B are constants. At the CURIE point therefore a and b become infinite, whereas they both vanish at the absolute zero; b is much smaller than a, as long as we do not come near the CURIE point (at 18° C. $b = 0.04\ a$).

The present paper relates to the susceptibility at temperatures below 0° C. down to very low temperatures — the boiling point of hydrogen — of the same nickel ring which was used by RADOVANOVITCH in his research; for the use of this ring we are indebted to the kindness of Prof. WEISS to whom we wish to record our thanks.

We wished in the first place to ascertain if the important deductions concerning magnetisation in the neighbourhood of the absolute zero to which the above formulae lead, are confirmed by experiment. From the more general point of view indicated above, it is also of importance to ascertain if all ferromagnetic magnitudes could be expressed *as functions of the saturation magnetisation.* And lastly the result can be of importance in the *physics of crystals*, for there are weighty reasons for ascribing ferromagnetic initial susceptibility to a *reversible turning of the direction of the magnetisation*, which is nearly the saturation magnetisation, in the elementary crystals. A knowledge of the initial susceptibility can therefore lead to a better grasp of the magnetic structure of the crystal itself.

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[1]) P. WEISS La rationalité des moments magnétiques moléculaires et le magnéton. Arch. de Genève (4)31 (1911), p. 401.

[2]) D. RADOVANOVITCH. Thèse Zurich (Université) 1911; also Arch. de Genève (4)32 (1911), p. 315.

[3]) LORD RAYLEIGH. Phil. Mag. March 1887, p. 225—245.

§ 2. *Experimental method and results.* We confine ourselves to a very short description of the research the details of which we shall publish in full later.

The ballistic method was used with the above-mentioned toroid, which was built up of circular plates of nickel. Absolute values were obtained by calibrating the galvanometer with a standard solenoid. The toroid, wrapped with its primary and secondary winding, was placed in a large silvered vacuum glass, into which a sufficient quantity of liquid gas was poured to ensure that the liquid surface of the bath was well above the toroid. The cryogenic part of the experiments gave rise to many serious difficulties on account of the large mass of metal which had to be cooled. For the measurements at liquid hydrogen temperatures the toroid was first immersed in liquid air in the cryostat; the air was then syphoned off, the cryostat evacuated and then filled with liquid hydrogen.

The numerical results are collected in the following table.

INITIAL SUSCEPTIBILITY OF NICKEL.

Bath	T	$\kappa_{H=0}$
Ordinary temp.	291°K.	3.045
Liquid oxygen	90	0.955
	76.5	0.881
Liquid hydrogen	20.5	0.782

Each of the values given above is the result obtained from measurements made with five fields between 0.017 and 0.090 gauss. The quantity b, which is extremely small even at ordinary temperature, at very low temperatures vanishes altogether within the limits of accuracy of the observations.

It is quite evident that with falling temperature a (or K) continues to decrease regularly. Just as with the value of b, the results as far as a is concerned leave no doubt of good *qualitative* correspondence with those obtained by extrapolation from the figures given by RADOVANOVITCH. As for the *quantitative* correspondence [1] it must be remarked that it cannot, from the nature of the case, be accurately tested; for it is a question of a difference between 1 and a figure which at very low temperatures differs from unity by a very small quantity. I and I_0 would have to be known with very great accuracy before we could be at all sure of the value of $\frac{I_0}{I} - 1$. Taking, however, the formula given by RADOVANOVITCH for a as a function of I to be correct, and using it to determine I from our results, we find that between 90° K. and 20° K. the saturation magnetisation does not increase much more than 0.0003, a result which is not inconsistent with the curve which seems to be suggested by the experiments concerning saturation magnetisation at low temperatures.

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[1] The difference between the absolute values at ordinary temperature obtained by RADOVANOVITCH and those given by us are caused by the change with time of the magnetic properties of the nickel toroid ("ageing", "Alterung", "vieillissement"). This change has been taken into account throughout our experiments.

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No. 127a.

* * *

W. J. DE HAAS. Isotherms of diatomic gases and of their binary mixtures. X. Control measurements with the volumenometer of the compressibility of hydrogen at 20° C.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, **26 April 1912,** p. 1422—1427.

EDUARD IJDO — PRINTER — LEIDEN.

Erratum Communication N⁰. 127*a*.

p. 3 line 2 from the top: for *vulumenometer* read *volumenometer*.

W. J. DE HAAS. — *Isotherms of diatomic gases and of their binary mixtures. X. Control measurements with the vulumenometer of the compressibility of hydrogen at* 20° C.

§ 1. *Introduction.* In Communication IX, "Control measurements with the volumenometer" (Comm. N⁰. 121*a*), a discussion based upon experimental data was given of the degree of accuracy attainable in determinations with the volumenometer. A determination of the compressibility of hydrogen at ordinary temperature has now given an additional desirable test of the accuracy with which the various experimental conditions in their mutual relationships have been fulfilled.

The investigation is based upon the Leiden measurements of the compressibility of hydrogen at pressures up to 60 atm. The accurate piezometers (Comm. N⁰. 50) and the sectional open manometer (Comm. N⁰. 44) specially designed by KAMERLINGH ONNES for that investigation rendered a very high accuracy attainable in those measurements. Considering this degree of accuracy, we may therefore take SCHALKWIJK's measurements with those apparatus at 20° C. to be quite accurate, and ascribe the small difference between his formula and that deduced from AMAGAT's results to a lower degree of accuracy in one or other of AMAGAT's measurements (perhaps in his determination of the normal volume, which can be done more accurately by KAMERLINGH ONNES's method). This conclusion is also supported by the fact that SCHALKWIJK's formula is confirmed by the results obtained by KAMERLINGH ONNES and HYNDMAN (Comm. N⁰. 78).

We may therefore write at 20° C.

$$pv_A = 1.07258 + 0.000667\, d_A + 0.00000099\, d_A^2,$$

in which p is the pressure, v_A the volume in terms of the normal volume and d_A is the reciprocal of v_A. On account of the small densities which occur in measurements made with the volumenometer (in which d_A is at the most 1.1) the d^2_A term may be neglected. The compressibility at 20° C. is then given by

$$\left.\begin{aligned} pv_A &= A_A + B_A\, d_A \\ \text{in which}\qquad A_A &= 1.07258 \\ B_A &= 0.000667 \end{aligned}\right\} \quad . \; . \; . \; . \; . \quad (I)$$

Again, on account of the small densities at which the volumenometer is used, the second of the terms on the right of the sign of equality plays but a small part in the result; it varies from 7.10^{-4} of pv_A at density 1.1 to 1.10^{-4} of pv_A at density 0.15. The question to be investigated in the proposed test was if compressibility determinations with the volumenometer could give values of pv_A to within 2.10^{-4}.

As appears from the table at the end of § 3 giving pv_A as obtained from experiment and d_A as calculated the accuracy attained in the compressibility determinations is as a rule somewhat greater than that which we desired (Comm. No. 121*a*, § 1). To show more clearly the nature of the remaining deviations, values of B_A determined by formula (I) have also been calculated from the volumenometer results by themselves; in doing this, of course, a sufficiently good approximation can be obtained only at the highest densities.

§ 2. *Summary of the experimental methods.* To get as good an idea as possible of the reliability of the volumenometer determinations of compressibility at temperatures between — 252° C. and — 259° C. the compressibility was first measured at ordinary temperature within the same pressure limits as would be chosen or were to be expected at the lower temperatures. Measurements were made with two distinct quantities of distilled hydrogen. For the first series a pressure of half an atmosphere was chosen as the starting point, and it was desired to ascend to a pressure of 1.1 atm. while in the second series the limits chosen were 0.16 atm. to 0.5 atm. The apparatus was filled in the usual way (cf. Comm. No. 94*f*) after repeated evacuations and washings with hydrogen.

For the determination at higher pressures measurements were made in the neck m_3 (see Plate I, Comm. No. 117) and pressures were obtained from the manometer θ_B—θ_F and the barometer

$\theta_C - \theta_D$. In this an artificial constant pressure practically equal to the barometric pressure was maintained in the manner usually adopted in the Leyden Laboratory by means of the ice pot *R*. To eliminate changes due to temperature fluctuations the four menisci to be observed were read twice in reverse order. Measurements were then made in the necks m_4 and m_5 (Pl. I loc. cit.). To do this the tap l_7 was closed, and, keeping k_4 closed, communication was established with a mercury pump through k_{41}, k_{43}. After careful evacuation the pressures of the volumes close to the necks m_4 and m_5 were measured, using the manometer as an indicator. For this two of the telescopes of the large Société Genevoise cathetometer were focussed upon the menisci in the volumenometer and manometer, and the heights were read each time from the standard meter *S*.

In an identical fashion measurements were made with a smaller quantity of gas in the necks m_3, m_4 and m_5.

For further experimental conditions and precautions reference may be made to Comm. No. 121*a*, § 4 and 5 and also to my dissertation which is to be published shortly.

§ 3. *Calculation and values of* pv_A.

The final value of the gas density for each of the two series of measurements, each with its own definite quantity of gas, was

TABLE I. H_2. Values of pv_A.

N⁰.	t	p	d_A calc.	pv_A obs.	O—C.
1	20° C.	0.46780	0.43603	1.07278	— 0.00009
2	»	0.58113	0.54162	1.07295	+ 0.00001
3	»	1.12867	1.05161	1.07328	
1	20° C.	0.16310	0.15205	1.07247	— 0.00021
2	»	0.20258	0.18885	1.07248	— 0.00022
3	»	0.39313	0.36645	1.07282	

obtained by means of equation (I) from the observed final pressure after the application of the correction necessary for the small difference between 20° C. and the temperature at which the measurements were made. The pressure coefficient used was 0.0036627 (Comm. N⁰. 60). On account of the smallness of the temperature difference for which a correction has to be applied no correction is needed for the dependence of this pressure coefficient upon the pressure. The observed volumes v_A for each measurement follow from the v_A's obtained from the final density and from the ratio of the volumes in each series measured at 20° C. to the final volume. Table I gives the values of pv_A, and those of d_A as calculated from p by means of equation (I).

From this it is evident that an accuracy of one in four thousand to one in five thousand is attained at the lower pressures, while in the series of measurements made at higher pressures the accuracy reached is greater than one in ten thousand.

§ 4 *Calculation of* B_A. From the former of the two series contained in Table I (pressures varying from 1.1 to 0.46) B_A can be calculated. Instead of $B_{A20^0} = 0.00067$ it gives

$$B_{A20^0} = 0.00074 \text{ so that } O-C = 0.00007,$$

in which only the fourth decimal is significant. In the second series the percentage error expected in B_A is too great to allow of a calculation of B_A itself. Only under more favourable circumstances could one count upon an accuracy of one in ten thousand or more in the values of pv_A; the error in pv_A becomes greater at smaller pressures; in B_A it is magnified four or five times and at small densities the utmost value of the whole term $B_A d_A$ for that series is 0.00026. In the meantime it may be remarked that a comparison of the positive differences found here between observation and calculation (+ 0.0013) with the corresponding positive difference in the first series seems to indicate a possible systematic error which makes its presence specially felt at the lower pressures 1).

In order to be able to compare the results obtained with others

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1) Possibly a small constant error arising from a change in the correction for the capillary depression since the control measurement of Comm. N⁰. 121*a*.

which just had in view the determination of the compressibility at ordinary temperature we must reduce the results to a common basis.

Take first the measurements made by LEDUC [1]) at 16° C. and at pressures varying from 1 to 1.5 atmospheres. From the numbers which he obtains from his experiments after the incorporation of other data for the compressibility at 0° C. we find to correspond with his result

$$B_{A20^\circ} = 0.0007 \text{ and therefore } O-C = 0.0000.$$

The figure last given does not necessarily lead to the conclusion that the Leiden determinations with the volumenometer are the less accurate. The degree of accuracy of LEDUC's results is indicated by the fact that he goes only to the fourth decimal place (for CO_2 CHAPPUIS [1]) and LEDUC differ by 0.0002). And the pressures used by LEDUC in this determination which is accurate to 1 in 10000 were very much more favourable (the smallest density was twice as great as that of the first series of Table I) than those which are experienced in experiments at liquid hydrogen temperatures and at which my measurements had to be made.

Determinations made by CHAPPUIS [2]) and by RAYLEIGH, in each case with apparatus designed to attain a higher degree of accuracy than that of the Leiden volumenometer, also afford a basis of comparison. CHAPPUIS measured compressibilities at 0° C. between 1.4 and 1.8 atmospheres. His results give $B_{A0} = 0.00058$, from which, using the figure given by KAMERLINGH ONNES and BRAAK [3]) for the difference between B_{A100° and B_{A0° we get

$$B_{A20^\circ} = 0.00064 \text{ and } O-C = -0.00003.$$

The values deduced from the two single observations distant by about half the pressure difference from each other, in which the errors are increased, differ by 0.0001.

Finally, Lord RAYLEIGH's [4]) measurements were made with an apparatus specially designed to give an accurate comparison between pv_A at half an atmosphere and its value at double that pressure.

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[1]) A. LEDUC, Recherches sur les gaz. 1898.

[2]) P. CHAPPUIS, Nouvelles études sur le thermomètre à gaz.

[3]) Comm. No. 100*b*.

[4]) Lord RAYLEIGH, Proc. Roy. Soc. 73 (1904), Z. S. physik. Chem. 52 (1905).

From them we get $B_{A10.7} = 0.00054$ from which, using again the Kamerlingh Onnes-Braak result just given, we obtain

$$B_{A20^\circ} = 0.00057 \text{ and } O—C = — 0.00010.$$

So that comparison between the results now given with those yielded by these different researches shows a satisfactory agreement.

In the proposed determination of B_A at hydrogen temperatures circumstances will be much more favourable than at ordinary temperature, for $B_A\, d_A$ will then be 15 to 20 times greater at the same pressure. We may regard the value obtained for B_A in this way at — 252°C. as accurate to within $2^0/_0$ and to within $10^0/_0$ at —259° C.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 127b.

W. J. DE HAAS. — Isotherms of diatomic gases and of their binary mixtures. XI. On determinations with the volumenometer of the compressibility of gases under small pressures and at low temperatures.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **25 Mei 1912** p. 85—91).

EDUARD IJDO — PRINTER — LEIDEN.

W. J. DE HAAS. *Isotherms of diatomic gases and of their binary mixtures.* XI. *On determinations with the volumenometer of the compressibility of gases under small pressures and at low temperatures.*

§ 1. *Criticism of the pressure equilibrium between the piezometer and the volumenometer.* In the investigation of the compressibility of hydrogen vapour with which a subsequent paper by Prof. KAMERLINGH ONNES and myself will deal, the volumenometer described in the previous Communication was used to measure the quantity of hydrogen contained under different pressures in a reservoir — the piezometer reservoir — which was immersed in liquid hydrogen and connected with the volumenometer by a capillary and tap. The pressure of the gas in the piezometer reservoir was then given for each measurement by the pressure of the gas in the volumenometer in pressure equilibrium with it. It was shown in Communications N⁰. 121*a* and N⁰. 127*a* that the accuracy with which the pressure, volume and temperature of the quantity of gas contained in the volumenometer could be determined was sufficient to allow of the evaluation of the virial coefficients B at low temperatures for hydrogen vapour from determinations of the compressibility of that vapour. More particular attention must now be bestowed upon the question of pressure equilibrium between the volumenometer and the piezometer.

In the course of the above experiments it was repeatedly necessary to adjust the mercury in the volumenometer to one of the lower necks (for instance, m_1, m_2, or m_4. Cf. Comm. N⁰. 117, Pl. I). The quantity of gas contained in the volumenometer was in those cases always less than that in the piezometer of 110 cc. capacity and at a temperature of —252° to —258° C., so that the gas in the piezometer was of a density from 12 to 20 times that in the volumenometer, but still not many times less. On each side of the capillary, therefore, which had to be long on account of the construction of the cryostat and narrow on account of the uncertainty of the volume correction to be applied for it, there are relatively large quantities of gas. On account of friction in the capillary, pressure equilibrium will be but slowly attained. From a preliminary experiment it was found desirable to be able to say from the measurements themselves when exactly this pressure equilibrium had been attained. In order therefore to obtain the necessary data for this, the behaviour of the pressure in the volumenometer was systematically observed during the final experiments upon the compressibility of hydrogen vapour at low temperatures (June 23 and 24, July 8, 14, and 18, 1911) on each occasion on which the meniscus was adjusted to one of the necks m_1, m_2, m_3, m_4 — this of course only after satisfying the experimental conditions to be fulfilled for equilibrium (regulation of cryostat and of volumenometer thermostat, constancy of room temperature). At intervals, as a rule every 5 minutes, the difference between the levels of the mercury in the manometer and in the volumenometer was read and corrected, from tables prepared beforehand, for changes occurring during the measurement in the quantities determining the corrections (such as change in the temperatures of the volumenometer, the piezometer, the dead-space, change in the capillary depression, etc.).

In this way the actual change in the difference between the pressure and the equilibrium pressure was known at all stages of the measurement. During the measurements a curve was drawn with this pressure difference as ordinate and time as abscissa, and the observation was regarded as at an end as soon as the plotted points began to fluctuate about a line drawn parallel to the abscissa axis The accompanying diagram (unit ordinate representing 0.1 mm. mercury) is taken from the above investigation and refers to the adjustment of the pressure equilibrium on July 18, 1911, an occasion on which circumstances were particularly unfavourable. The observed pressure differences, increased by a certain fixed quantity, are represented by circles. At the end of § 3 we shall return to this diagram.

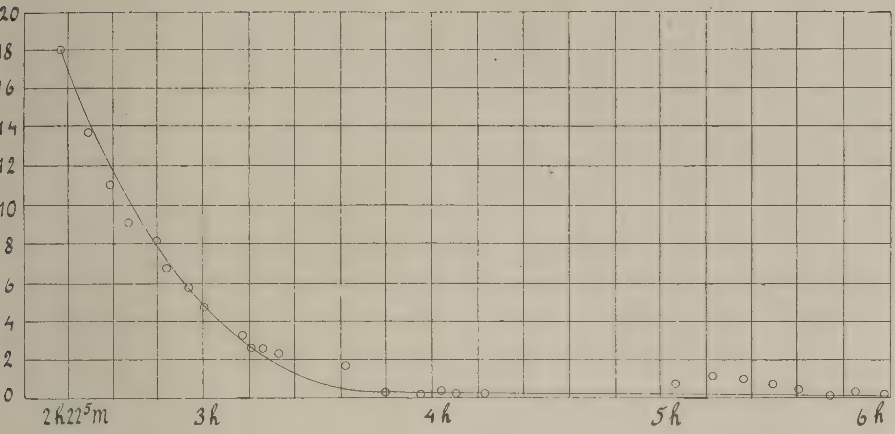

Fig. 1.

§ 2. *Calculation of the pressure change from the experimental data.*

The curve giving the change in the pressure difference between the two communicating vessels as a function of the time was now calculated from the dimensions of the apparatus and from data determining the temperature distribution along the glass capillary. As will be seen from the end of § 3, calculation is in complete agreement with observation, and is therefore suitable for checking the smallest pressure difference experimentally determined by the above method in the case discussed in § 3. The reduction of the theoretical calculation to formulae has the result that it not only covers this particular case, but it can also be applied to gauge the degree of pressure equilibrium in similar cases in which capillary connections occur in experiments at low temperatures.

The influence of gravity upon the gas is left out of account in the calculation, as is also the pressure difference which KNUDSEN's researches show must exist. If necessary both corrections may be applied to the observed pressure at which equilibrium is attained [1]).

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[1]) As a general rule, however, both corrections may be neglected. For the lowest pressure occurring in the course of the experiments for which this calculation was made the KNUDSEN correction just reached that limit at which the calculations by KAMERLINGH ONNES for the capillaries of his hydrogen and helium thermometers show it would begin to be appreciable.

The influence of slipping along the walls of the capillary is also left out of account, while the volume of the capillary has been regarded as negligible compared with that of the reservoir and of the volumenometer. It is also assumed that the speed may be regarded as to remain the same over a short period of time, and that the speed is small (far below the critical); further that the temperature, T, and the pressure, p, may be regarded as uniform over any cross-section, so that if x is the length and y and z two axes at right angles to it and to each other, p is independent of y and z; and, finally, that the speeds v and w in the directions of y and z may be taken to be zero. A flow is therefore assumed such that in a tube at constant temperature throughout and for a substance whose density is independent of the pressure **Poiseuille**'s law should hold, and such as may be regarded as subject to this law over any element of length, dx, of the capillary when the values of the pressure gradient, the density ρ and the viscosity η at that particular place are inserted. Working out the equations of motion subject to the given assumptions [1]) at once leads to the result

$$\frac{dm}{dt} = \frac{\pi}{8} R^4 \frac{\rho}{\eta} \frac{dp}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where m is the mass of the gas contained in the reservoir, and hence $\frac{dm}{dt}$ the mass which flows per unit time across any section of the capillary.

We assume η to be independent of the pressure so that $\eta = f(T)$, and for $f(T)$ we take **Sutherland**'s formula

$$\eta = \eta_0 \frac{1 + \frac{C}{273}}{1 + \frac{C}{T}} \sqrt{\frac{T}{273}}$$

in which C is a constant. As an approximation for vapours we may write $p = a\rho + b\rho^2$ in which a and b are functions of T. These and all other quantities occurring in the present calculation were expressed in absolute measure (the C. G. S. system was chosen). If T be given as a function of x, equation (1) can at once be integrated.

As a further simplification for this integration we shall regard

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[1]) Cf. O. E. **Meyer**, Pogg. Ann. 127. p. 253, 353.

b as negligible on account of the smallness of $b\rho^2$ compared with $a\rho$. If the pressure difference between the ends of the capillary is small, deviations from BOYLE's law may, to the same extent, be allowed for. For further information on this point I may refer to my dissertation.

It may be further remarked that we may differentiate between three different portions of the capillary. The first part projects above the cryostat, and has throughout its whole length the same temperature, that of its surroundings (room temperature); for the pressure at the upper end of this portion we shall write p_4 and for the pressure at the lower end p_3. In the second part of the capillary the temperature changes from the room temperature to that of the cryostat bath. The pressure at the upper end of this part is p_3, and for the pressure at the lower end we shall write p_2. The third portion of the capillary is wholly within the cryostat bath, and over its whole length has the temperature of the bath. p_2 is the pressure at the upper end, and we shall write p_1 for the pressure at the lower end.

With the object above indicated of not only calculating for the particular case discussed in § 3, but also of obtaining simple formulae applicable to analogous cases I have endeavoured to find a simple form for the function expressing the temperature of the middle portion in terms of the length; in order that four terms in this would suffice I have imagined a sudden change in the temperature at the junction of the second and third portions of the capilary, in other words I assume that at that point the temperature changes rapidly over a length which is large compared with the diameter of the capillary but is still small compared with its length.

The calculation is therefore made for a temperature distribution other than that which actually exists, but, as will be seen, the difference between the two cases does not affect the result

The temperature distribution over that portion of the capillary in which the temperature is variable is thus represented by

$$x = q + l_x T + m_x T^2 + n_x T^3 \quad . \quad . \quad . \quad . \quad (2)$$

In the experiment further discussed in § 3 the temperature change at the surface of the bath would be one of from $T_2 = 26°$ K. to $T_1 = 15°$ K.

With $a = a_1 T$,

$$k = \frac{1 + \frac{C}{273}}{\sqrt{273}} \text{ and } A = \frac{8}{\pi R^4}\frac{dm}{dt}, \quad . \quad . \quad . \quad . \quad (3)$$

(1) now gives

for the first portion $$A = \frac{1}{2\lambda_4 \eta_4 T_4}(p_4^2 - p_3^2), \quad . \quad . \quad . \quad . \quad (4)$$

and for the third portion $$A = \frac{1}{2\lambda_1 \eta_1 T_1}(p_2^2 - p_1^2), \quad . \quad . \quad . \quad (5)$$

while the substitution of

$$T = C \operatorname{tg}^2 \alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

gives

$$p_2^2 - p_3^2 = 4Aa_1 k\eta_0 C^{5/2}[(F_T)_2 - (F_T)_3] \quad . \quad . \quad . \quad (7)$$

in which

$$F_T = \left[\frac{nC^2}{3}\operatorname{tg}^9 \alpha + \frac{C(2m - 3nC)}{7}\operatorname{tg}^7 \alpha + (l - 2mC + 3nC^2)\left(\frac{\operatorname{tg}^5 \alpha}{5} - \frac{\operatorname{tg}^3 \alpha}{3} + \frac{\operatorname{tg} \alpha}{1} - \alpha\right)\right], \quad (8)$$

so that p_2 and p_3 can be expressed in terms of p_1 and p_4. From (4), (5), (7) it is seen that for a case such as that discussed in § 3 for which $T_1 = 15$°K. and $T_4 = 295$°K., p_1 does not differ appreciably from p_2, so that one need not be very particular about the lower limit in the integral of (7) and (8), and the small jump in the temperature is of no influence within the limits of accuracy desired; this indeed is otherwise obvious if one considers that the gas flows about 20 times more slowly in the cold portion while the viscosity is also about as many times smaller.

With the temperature function now obtained for the interchange of pressure in a gas of known C, η_0 and a, through a capillary of radius R, and for a given temperature distribution, we obtain

$$\frac{dm_2}{dt} = \frac{\pi R^4}{8 K a_1}(p_1^2 - p_4^2), \quad . \quad . \quad . \quad . \quad (9)$$

in which m_2 is the mass of gas in the volumenometer, and

$$K = L\eta_0 (F_{T_2} - F_{T_3}) + M\eta_1 \lambda_1 T_1 + N\eta_4 \lambda_4 T_4,$$

where the quantities L, M and N follow at once from (4), (5) and (7). The first member of the expression for K refers to the portion of the capillary in which the fall of temperature occurs, and the second and third members to those portions in which the temperature is uniform.

If we further write

$$p_1 = a_1\, T_1 \frac{m - m_2}{v_1}, \qquad p_4 = a_1\, T_4 \frac{m_2}{v_2}, \quad . \quad . \quad . \quad (10)$$

in which v_1 represents the volume at the lower temperature, v_2 that at ordinary temperature, and m the total mass, and then integrate (9) we obtain, with the omission of an integration constant

$$\frac{v_1\, v_2}{T_1\, T_4\, m} \log \frac{(m - m_2) + \dfrac{T_4 v_1}{T_1 v_2} m_2}{(m - m_2) - \dfrac{T_4 v_1}{T_1 v_2} m_2} = \frac{\pi R^4 a_1}{4\,K} t. \quad . \quad (11)^{1)}$$

The case discussed in § 3 and graphed in fig. 1 gives an example of the curves given by this equation.

§ 3. *Application to a special case. Deductions.*

From measurements made during the experiment of 18th July 1911 temperatures were to be taken as

	—258° C.	for	10 cm. in the liquid bath
	—228°	„	7 cm.
	—115°	„	7 cm.
	— 25°	„	14 cm.
Room temp. at	+ 22°	„	22 cm projecting outside the cryostat.

For the calculation of (2) the temperature of each portion is regarded as the temperature at its centre.

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1) In the simple case in which $p_1 + p_2$ may be regarded as constant, and $T_1 = T_4$, $m = v_1\, d + v_2\, d$ in which d is the common density in both vessels and substitution of (10) in (11) give

$$\frac{v_1\, v_2}{C_1\,(v_1 + v_2)} \log \frac{C_2}{p_1 - p_2} = C_3 t.$$

The subscript 4 is here replaced by 2.

This is the formula given by RAYLEIGH, Scientif. papers Vol. IV 1892—1901 p. 53. This formula does not hold for instance for the evacuation of a vessel by a pump through a capillary, to which (11) is applicable as long as the pressure is not so small that the mean free path becomes comparable with the diameter of the capillary.

We therefore get $\lambda_1 = 10$, $\lambda_4 = 11$, $T_1 = 15$, $T_4 = T_3 = 295$; and from $x = 10$ to $x = 49$ equation (2) holds with the values

$$q = 1.66, \quad l_x = 0.389, \quad m_x = -0.00278, \quad n_x = 0.00000682\,;$$

while, as was already remarked, the temperature jump assumed to take place at the surface of the liquid has no influence upon the result. We also find

$$m = 0.017, \ v_1 = 110, \ v_2 = 1035.$$

The line drawn in fig. 1 has been calculated from these data. The observed pressures, indicated by circles, agree well with the results of calculation.

Between half-past four and five more liquid gas was admitted into the cryostat. The readings during which the resulting pressure interchange was stopped by means of a valve are not marked in the figure. A slight temperature fluctuation occasioned by the refilling is clearly seen in the diagram. A small pressure increase at 5^h5^m dies down about six o'clock quite in accordance with the calculated curve. (See 3^h27^m. At this point the temperature also increased).

As can be seen, it took more than an hour for the last 1.8 m.m. pressure difference to die down to 0.02 m.m. (the whole pressure was 5 cm).

The calculations show that the assumed distribution of temperature along the capillary is, in the main, correct. It gives a very welcome estimate of the time requisite for the last appreciable interchange of gas.

To establish pressure equilibrium as rapidly as possible in such experiments it is necessary that:

1. as little of the capillary as possible should project above the cryostat, and that the stem within the cryostat should be kept as cold as possible;

2. the upper part of the capillary should be wider than the lower, as is the case, for instance, in the helium thermometer of KAMERLINGH ONNES, or better still, the connecting capillary should be gradually narrowed. (In fig. 5 of Suppl. N°. 21*b* compare the tube which, in the experiments by KAMERLINGH ONNES on the attainment of the lowest possible temperatures, had to carry off helium vaporised under a pressure of 0.2 mm. with the least possible reduction of pressure; the dimensions of this tube were calculated according to the principles of § 2).

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H. KAMERLINGH ONNES.
Director of the Laboratory.

No. 127c.

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H. KAMERLINGH ONNES and **W. J. DE HAAS.** — Isotherms of diatomic substances and of their binary mixtures. XII. The compressibility of hydrogen vapour at, and below, the boiling point.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **25 Mei 1912,** p 92—101, **29 Juni 1912,** p. 282—283).

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H. KAMERLINGH ONNES and W. J. DE HAAS. *Isotherms of diatomic substances and of their binary mixtures.* XII. *The compressibility of hydrogen vapour at, and below, the boiling point.*

§ 1. *Introduction.* To the region covered by the investigations which have been made for many years past in the Leiden laboratory upon the equation of state for hydrogen at low temperatures (for the latest paper see Comm. N°. 100*a*, Nov. 1907) the present Communication adds the region for hydrogen vapour lying between — 252° C. and —258° C. While the lowest reduced temperature attained in the measurements of KAMERLINGH ONNES and BRAAK was about $\mathfrak{t} = 2.2$, in our present investigation we were able to calculate the second virial coefficient B for the further region from $\mathfrak{t} = 0.7$ to about $\mathfrak{t} = 0.5$; by this means, since interpolation between $\mathfrak{t} = 0.7$ and $\mathfrak{t} = 2.2$ is not a matter of any difficulty, B becomes known over a very extensive region of reduced temperature (from $\mathfrak{t} = 0.5$ to $\mathfrak{t} > 12$). The second reduced virial coefficient is therefore known for a single substance over a much more extensive region of temperature than has hitherto ever been the case. This extension was especially to be desired as, in the first place, it allows a better comparison from the point of view of the law of corresponding states of B for hydrogen with its value for various other substances and this will become of particular importance when the comparison can be extended so as to embrace monatomic substances (a communication by KAMERLINGH ONNES and CROMMELIN will shortly appear dealing with the B for argon at low reduced temperatures). In the second place it allows us to put to the test theoretical deductions concerning B (for instance, the connection between the peculiarities of B with the peculiarities of the specific heats and of viscosity, and also of the dielectric constants and of penetrability by electrons). This is all the more important as B is related to that state which according to REINGANUM can be called the *planetary* gas state in which, in allowing for the influence of collisions between molecules, only two molecules need be considered, as the possibility of the proximity of others may be neglected.

From B, moreover, one can calculate the experimentally determined corrections of the hydrogen thermometer scale to the AVOGADRO-scale, which have hitherto been known only down to — 217° C., down to the lowest temperatures which can be measured with the hydrogen thermometer. (Cf. Comms. Nos. 101*b* and 102*b*).

The uncertainty in the adjustment of a cryostat bath to an accurate definite temperature and in the measurement of that temperature is much greater than that with which a temperature, once steadied, can be maintained constant. Since, now, uncertainty in the determination of the temperature is of great influence upon the values of B obtained from the observed pv_A, it was decided to proceed with isothermal measurements so as to be as independent as possible of thermometrical measurements. A further advantage of constancy of temperature in the comparison of values of pv_A at different pressures lies in the circumstance that the possible difference between the temperature of the gas in the piezometer and that of the thermometer in the bath is constant throughout. The advantages of isothermal measurements would have been far greater for us had we not frequently been obliged to aim at obtaining the same reading of the resistance thermometer instead of at the maintenance of a definite temperature.

The investigation was carried out at three temperatures, approximately — 252°.6 C., — 255°.5 C. and — 257°.3 C. A lower temperature than — 257°.3 was not desirable as the smallest pressure to be measured at this temperature had already sunk as low as 5 cm. and further progress in this direction would have necessitated another apparatus.

For each isotherm the densities were so chosen that the ratio of the extreme densities was about two to one in each case. By this means it was brought about that in the solution of B_A from the two equations

$$pv_{A_1} = A_A + B_A\, d_{A_1} + C_A\, d_{A_1}{}^2$$
$$pv_{A_2} = A_A + B_A\, d_{A_2} + C_A\, d_{A_2}{}^2$$

the coefficient of B_A was approximately 1. In this solution C_A was taken as a correction term from the equation of state VII. H_2. 3 (formula (16) Comm. N⁰. 109*a*).

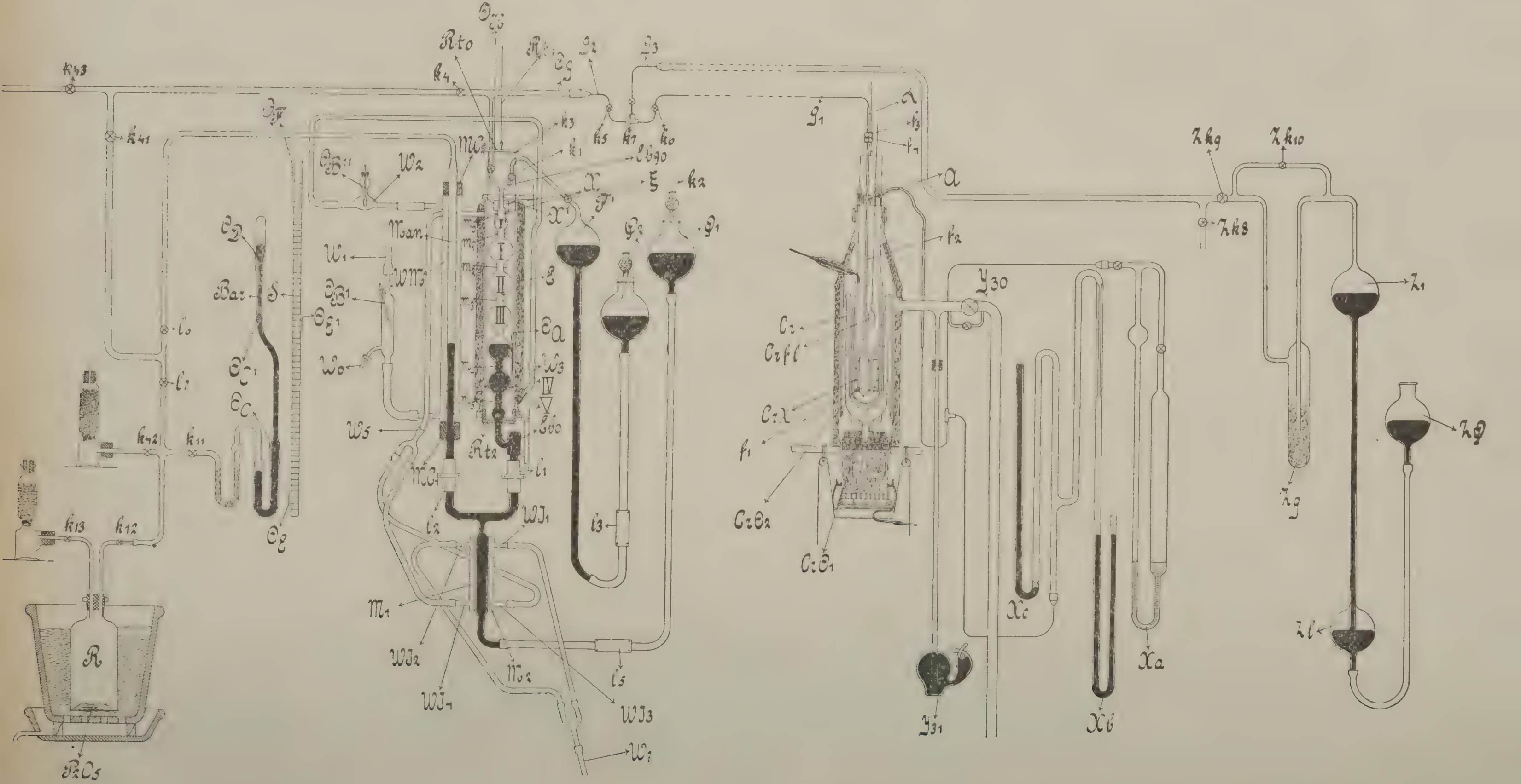
k43
k41
k42
k11
k13
k12
l0
l1
R
P2O5
Bar
Ɛ
Rto
k4
k3
k1
k5
k7
k0
k2
MC2
W2
W1
W0
W5
W7
Man1
I
II
III
IV
V
Rt2
MC1
WI1
WI2
WI3
WI4
M1
Mo2
l2
l3
l5
l1
X
X'
F'
Ξ
g1
Ca
W3
f1
f2
f3
f4
a
Y30
Y31
Xa
Xb
Xc
Zk8
Zk9
Zk10
Z1
Zl
Zg
ZQ

Fig. 1

Finally, for practical reasons, it was necessary to remain as far as possible away from the region of condensation, as a sudden fluctuation of the temperature could quite well occasion condensation to take place upon the walls of the piezometer, and particularly of the capillary, and this, in view of the excessively slow liberation of liquid and vapour from the glass, would render the measurements valueless.

The measurements were made with a piezometer immersed in a bath of liquid hydrogen and connected through a capillary with the volumenometer studied in detail in Comm. N⁰. 127*a* (see fig. 1, p. 23). The piezometer was first evacuated and a quantity of gas measured in the volumenometer; the valve between the two was then opened. Pressure equilibrium was then allowed to establish itself at the desired value, and then the pressure and the quantity of gas remaining in the volumenometer were determined.

§ 2. *Arrangement of experiments. Auxiliary apparatus.*

The experimental arrangements are shown in fig. 1, p. 23 [1]). One portion of the apparatus had already been utilised in the investigation of the diameter for oxygen, and is described in Comm. N⁰. 117. The left hand part of fig. 1, p. 23, is an improved copy of the left hand part of Pl. I of that Communication, to which we may in the first place refer. The improved diagram embraces the modifications which were introduced later, and which are described in Comm. N⁰. 121*a*. Identical parts are indicated by the same letters in fig. 1 and in Comms. Nos. 117 and 121*a*, parts which have undergone modification are distinguished by accents, while parts which are new or are now lettered for the first time have new letters attached to them We may refer to W. J. DE HAAS's thesis for further details concerning the water circulation, *W*, which, supplied from the thermostat, keeps constant and uniform the temperature of the volumenometer and of the manometer.

The volumenometer is connected to the auxiliary reservoir F'' through the taps k_1 and k_2. This allows one to add gas to the measured quantity contained in the volumenometer, or to temporarily abstract a measured quantity from the volumenometer. This was essential in our experiments as the volume of the piezometer, in which the gas density was sometimes practically 20 times as great as that in the volumenometer, was 110 c.c. and that of the volumenometer was not more than 1250 c.c. Hence, if, for instance, the volume is adjusted to the smallest volume in the volumenometer (the neck m_0 in the figure) at a pressure of one atmosphere, then even when the volumenometer is completely filled (to the neck m_5 in the figure) the second equilibrium pressure of half an atmosphere, which, according to § 1, is desirable in this case, is not yet attained The admission of gas from the volumenometer to F' and vice versa can be of use in another way, viz. in the transition to another temperature and in the adjustment of pressure equilibrium In the course of our experiments, however, we have not been able to make such free use of the auxiliary reservoir as we should have liked. The volumenometer can be evacuated through the valves k_3, k_4, k_{43}; and it can be connected to the barometer and to the constant pressure reservoir, R, (Comm. N⁰. 60, Pl. VI) through k_3, k_4, k_{41}, l_7, k_{11}, k_{12}. When the volumenometer adjustments and the value of the pressure permit of it, the valve l_7 may be closed and the pressure then determined from the manometer M alone, the space above which is then evacuated through l_6. We may refer to Comm. N⁰. 121*a* by W. J. DE HAAS for further details concerning the pressure measurement.

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[1]) In the drawing some details of no importance are incorrectly represented, viz: the ice ought to cover the bottle *R*, the air-trap *Zl* is in reality much smaller, the safety-tube Y_3 is of course not wholly filled with mercury.

To ascertain when pressure equilibrium has been attained we applied the method already described in Comm. N⁰. 127*a*; the pressure in the volumenometer was under constant observation, and from the curve expressing the pressure as a function of the time, we deduced, during the observations, the time at which the pressure difference originally existing between the volumenometer and the piezometer had sunk to a value that was insignificant. The reliability of this method is shown by the calculations published by W. J. DE HAAS in Comm. N⁰. 127*a*. For assistance rendered in the application of this method and for further help given in the course of this research we should like to express our indebtedness to Mrs. DE HAAS-LORENTZ.

Readings were taken with a very fine Société Genevoise cathetometer with three telescopes[1]), each with a micrometer eyepiece and level. A scale with very accurate subdivisions (Comm. N⁰. 60) was used for the readings with the micrometer eyepieces.

Communication between the volumenometer and the piezometer (see the right hand portion of the diagram) was obtained through the tap k_3, the glass T-piece (closed on the other side by k_4) over which a connecting tube is cemented, a copper capillary g_2 (to give a certain elasticity to the connections), the steel taps k_5, k_6, a steel capillary g_1 and a glass capillary f_2. The steel taps k_5, k_6, k_7, were provided with selected cork packing and were kept for about half an hour at a pressure of 50 atm. They closed perfectly. Connections between steel and glass capillaries were also made with the greatest care. This connection was made by means of a brass screw soldered to the glass capillary, the capillary being very slightly rounded and projecting about $^1/_4$ mm. beyond the screw; this joint sustained a high vacuum for a long time. The rounded end of the glass capillary was covered with a packing ring made of fibrous plate, and could be screwed with force into the brass nut soldered to the steel capillary.

The diagram does not show the wool with which all the principal parts of the apparatus were wrapped. The barometer was wrapped with the greatest care in wool, and was, moreover, surrounded by a double layer of paper so as to eliminate all convection currents. Neither are the numerous thermometers shown in the diagram which were suspended along the whole apparatus.

Finally, the connections Zk_9, Zk_{10} lead to the hydrogen reservoir Z_1. To this reservoir is attached a side tube with a valve, Zk_8, through which the whole apparatus can be filled with hydrogen; it is also provided with a purifying chamber Zg, through which the gas passes on its way to the measuring apparatus and consisting of a tube filled with glas wool surrounded by a DEWAR flask containing liquid air. After the measurements the gas can be collected in Z_1 through Zk_9, Zk_{10}.

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[1]) Compare the similar adjustments of Comm. N⁰. 95*e*, Table I.

The difference between the levels of the top and the edge of the meniscus and between the top of the meniscus in one of the necks and the central line on a screen (cf. Comm. N⁰. 84, Pl. II) can be obtained with sufficient accuracy and more quickly from the catethometer scale than with the standard scale and level and the micrometer eyepiece. In the majority of cases it is sufficient and much simpler still to estimate these differences of level from the standard scale without focussing the micrometer upon the divisions of the standard scale at all. For an error of 10% in the determination of the height of the meniscus leads to an error of 1% in the capillary depression; and an error of 1 mm. in the estimation of the height of a line on the screen induces an error of only 16 or 17 mm³. in the volume, which makes a difference of only 1 in 60,000 in the volume of gas usually employed.

We may refer to Comms. Nos. 83, 94*c*, 94*d*, 94*e*, and 121*a* for descriptions of the thermostat, the water circulation and the cryogenic bath and auxiliary apparatus.

§ 3. *The hydrogen.* The apparatus was filled with distilled hydrogen by means of the arrangement described in Comm. N°. 94*e*, § 2; the tap Zk_9 (see fig. 1) was utilised for the repeated evacuations and washings with hydrogen.

§ 4. *The temperatures.* The thermostat supplied the water circulation, *W*, with water at very uniform temperature. (See Comm. N°. 121*a*).

Stirring was continuous during the measurements. A thermometer divided into 20-ths of a degree and calibrated by the Reichsanstalt was attached to the stirrer of the volumenometer, the mean temperature being thus obtained. The influence was studied beforehand of fluctuations in the room temperature upon that of the water in the jacket surrounding the volumenometer, and it was found sufficient to keep it constant to within one deg. Cent. This was always done. (For further details see dissertation by W. J. DE HAAS). Every determination of the volumenometer temperature can then be regarded as certain to within 0°.02 C.

The temperature of the cryostat was regulated in the usual way; great care was devoted to keeping it constant by Mr. G. HOLST, whom we wish to thank for his assistance. It would take up too much space here to give all the curves of this temperature regulation, but as an example we may state that in the determination of the isotherm at — 255°.5 C., made on the 24th June, and on the 8th and 14th of July, 1911, the values of the differences at five points from the first determination were

0.005, 0.012, 0.010, 0.000 degrees Centigrade.

This corresponds to an uncertainty of 0.00004 in the value of pv_A.

The temperature of the bath was furnished by the determinations themselves. See § 6.

§ 5. *Calibration, constants and calculation of corrections.*

a. *Pressures.*

The corrections, and in particular the optical corrections, for the apparatus have already been discussed in part in Comm. N°. 121*a*.

The pressures were always reduced to the normal atmosphere of 45° N. For this the value of the Leiden atmosphere, 75.9463 [1]), was used. The following corrections were applied to the pressures:

1. A temperature correction for the inequality between the temperatures of the mercury in the manometer and in the volumenometer (Comm. N°. 121*a*).
2. A correction for the standard meter which is 999.91 mm. at 0° C. (Comm. N°. 70).
3. An optical correction for the refraction of light by the glass windows (Comm. N°. 121*a*) and by the manometer tube.
4. A correction for the capillary depression. These corrections were tabulated for various widths of tube, being obtained from KELVIN's graphical construction and from LOHNSTEIN's [2]) formula.
5. A correction for KNUDSEN's transpiration pressure [3]).
6. A correction, where necessary, for the pressure of the air column between the lower barometer meniscus and the manometer meniscus.
7. A correction for the aerostatical difference between the pressure in the volumenometer and that in the piezometer was neglected.

A discussion of the degree of accuracy attained in the determination of the pressure has already been given in Comm. N°. 121*a*.

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[1]) This value has been calculated with the number for the gravity at Leiden used in Comm. N°. 60, Sept. 1900, p. 304, and $g_{\text{norm}} = 981.625$ according to Suppl. N° 23, „Einheiten" *a*.

[2]) F. LOHNSTEIN. Ann. d. Physik (4) 33 (1910), n°. 2.

[3]) M. KNUDSEN. Ann d. Physik (4) 31 (1910), n°. 3.

b *Volumes.*

Reference may be made to Comm. N⁰. 121*a* for the calibration of the volumenometer.

The volumes as measured were always corrected at their calibration temperature. This correction was always very small.

A correction for the compression of the glass vessels was applied by means of the formula

$$\frac{\delta V}{V} = {}^3/_2 \frac{(1-\mu)}{E} \frac{(p_i - p_e)}{d} R$$

in which $E = 6500$ K.G./mm^2, $\mu = {}^1/_4$, $R = 3.9$ cm., $d = 0.5$ mm. (See Comm. N⁰. 88).

In the calculation of the volumes, the volumes of the mercury menisci were taken from the table given by SCHEEL and HEUSE [1]).

As regards the accuracy of the volumes measured we may remark that a variation of one degree in the temperature causes a change of only 1 in 40000 in the volume. The correction for the compression gives $\frac{1.3}{10000}$ for $\frac{\delta V}{V}$ at the lowest pressure measured (5 cm.). If this correction is applied, the remaining uncertainty is certainly less than $^1/_{10000}$.

As regards the volume of the mercury menisci as, for instance, in the case of $2R = 14.8$ mm. where the volume is 179.4 mm^3. for a meniscus height of 1.6 mm., and 192.2 mm^3. for a height of 1.7 mm., the error for heights lying between these two values is certainly not so great as 10 mm^3. This is certainly negligible in a volume which would, at ordinary temperature, be at least 1200 cm^3., seeing that the volume of the piezometer is 110 cm^3. and contains gas of density from 12 to 20 times that in the volumenometer. The same may be said of the uncertainty in the volume of the dead space. Such portions of this as were not separately calibrated with mercury (steel and glass capillary, see dissertation DE HAAS) were volumenometrically calibrated. The total dead space was about 10 cm^3. An error of 1 $^0/_0$ in the calibration or of 3 degrees in the temperature causes an uncertainty of 100 mm^3. This is only 1 in 12000 of the 1200 cm^3. just mentioned. The volume calibration, however, was much more accurate, while, as was stated above, the room temperature was kept constant to within a degree.

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[1]) K. SCHEEL and W. HEUSE. Ann. d Phys. (4) 33 (1910), n⁰. 2.

These comments are also all applicable to the determinations of Comm. N^0. 121*a*.

The accuracy attained in the calibration of the piezometer was greater than 1 in 10000 (cf. dissertation DE HAAS). The volume was corrected for the temperature of the cryostat by means of the formula

$$v_t = v_0 \left[1 + \left\{ k_1 \frac{t}{100} + k_2 \left(\frac{t}{100}\right)^2 \right\} 10^{-6} \right]$$

in which

$$k_1 = 2343$$
$$k_2 = 272$$

(See Comm. N^0. 95*b*, § 1). The error arising from this method can only be very small.

Temperature corrections for the gas in the glass capillary were applied in the manner published in Comm. N^0. 97*a* § 8. For this, the temperature distribution along the stem was taken from Comm. N^0. 95*e*. That this temperature distribution is approximately correct was apparent, moreover, from the time it took pressure equilibrium to be established. Cf. Comm. N^0. 127*a*.

Collecting all these, we may regard the volumes occupied by the cooled gas as certain to within 1 in 10000. Allowing for what we have already stated regarding the pressure, but not taking temperature uncertainty into account, we may expect an accuracy of 0.00002 in the pv_A's, or, at the highest pressure to within one fivethousandth, and at the lowest pressure, to within $^1/_{2500}{}^{th}$ of the value of pv_A.

§ 6. *Calculation and Results.* The quantities of gas were always expressed in terms of the normal volume. For this purpose equation I of Comm. N^0. 127*a* was used:

$$pv_{A20^\circ C} = 1.07258 + 0.000667\, d_{A20^\circ C}.$$

Using, where necessary, an approximate temperature as a correction factor for the piezometer, the measurements yielded values of d_A, the density of the gas in the piezometer under the observed pressure. The temperature of the gas in the piezometer for each series was obtained from the pv_A itself for that particular series. For that purpose values of C_A in

$$pv_A = A_A + B_A d_A + C_A d_A^2$$

Errata Communication N⁰. 127.

p. 31 table I line 7 from the bottom: for „0.10964” read „0.10864”.
p. 31 „ I „ 6 „ „ „ „ „0.063469” „ „0.063489”.
p. 31 „ I „ 6 „ „ „ „ „0.000031” „ „0.000051”.
p. 31 „ I „ 1 „ „ „ „ „0.057104” „ „0.057110”.
p. 32 line 2 from the top: „ „0.00489” „ „0.000489”.
p. 32 table II „ „—253°.63” „ „ —252°.60”.
p. 32 „ II before the values of B_{At} insert the sign „—”.

were used in the calculation which were obtained for each (at first approximate) temperature from the special reduced equation of state for hydrogen VII . H_2 . 3 given in Comm. N^0. 109*a* equation (16) which was deduced from the observations of Kamerlingh Onnes and Braak and adjusted to a temperature of —217° C. A_A and B_A then follow from our observations and also pv_A at the same temperature for the density of the gas in the hydrogen thermometer of 1100 mm. zero pressure. From this with

$$(pv_A)_{t_S} = (pv_A)_0 \, (1 - 0.0036627 \; t_s)$$

we finally obtain the temperature on our hydrogen thermometer of 1100 mm. zero pressure.

The temperatures obtained in this way yield a calibration on the hydrogen scale of the resistance thermometer whose readings serve as a guide to the regulation of the temperature of the bath. This resistance thermometer was also calibrated with the hydrogen thermometer independently. The two calibrations are not quite in agreement. A subsequent paper by Kamerlingh Onnes and Holst will return to the question of this difference.

We obtained (where t_s is the temperature on our hydrogen thermometer of zero pressure 1100 mm.):

TABLE I. H_2. Values of pv_A.

Series	N^0.	t_S	p	d_A	pv_A	O—C
I. 23 and 29 June 1911	1	—252°.63	0.34786	4.7568	0.073129	
	2		0.60358	8 4597	0.071348	
II. 24 June 8 and 14 July 1911	1	—255°.46	0.10964	1.6918	0.064216	
	2		0.20672	3.2560	0.063469	0.000031
	3		0.27759	4.4133	0.062898	0.000012
	4		0.31318	5.0026	0.062603	0.000008
	5		0.31294	4.9992	0.062598	
III. 14 and 18 July 1911	1	—257°.26	0.06698	1.1582	0.057834	
	2		0.13153	2.3031	0.057104	

The second series was represented by

$$pv_A = 0.065043 - 0.00489\, d_A + C_A d_A^2$$

deduced from Nos. 1 and 5, with C_A as before, and the column O—C gives the differences between observation and calculation. These differences are smaller than those corresponding to the observed temperature fluctuations of the bath (see § 4) which is in agreement with the assumption that it is the mean temperature of the bath which must be taken as the temperature of the gas in the piezometer. This series also supports the use of the assumed C_A. Series I and III, lacking the controls possessed by series II in itself, are less reliable. Various circumstances have obliged us to postpone our experiments for some time to come, so that for the temperatures of series I and III we have not been able to give such extensive series of measurements as in series II.

From Table I we finally obtain:

TABLE II.

H_2. Individual virial coefficients B_A for hydrogen vapour

t_s	B_{At}
— 252°.63	0.000481
— 255°.46	0.000489
— 257°.26	0.000638

§ 7. *Smoothed values of the virial coefficients, and corrections of the international hydrogen thermometer to the absolute scale*

These corrections are to be determined from the virial coefficients B_A by the method employed by KAMERLINGH ONNES and BRAAK in Comm. N⁰. 101*b*. For this, however, it is desirable to use smoothed values. This was tried by plotting log B as a function of log T. Taking account of the accuracy of the various measurements there seemed to be much to recommend the smoothing given in Table III (in which the temperatures $\theta = T - 273.09$ are given in KELVIN degrees, Table IV having been used for the calculation).

TABLE III.

H_2. Smoothed virial coefficients B_A for hydrogen vapour.

θ	B_{AT}
— 252°.47	— 0.00047
— 255°.32	— 0.00049
— 257°.10	— 0.00055

In Table IV these values of B_{AT} have been used to supplement by data for — 252° C., — 255° C. and — 257° C. the list given in Comm. N⁰. 101*b* of experimental corrections $\Delta t_i = \theta - t_i$ of the international hydrogen thermometer to the absolute scale.

TABLE IV.

Corrections of the international hydrogen thermometer to the absolute scale.

t_i	Δt_i in degrees K.
— 252°.59 C.	+ 0.118
— 255°.45	+ 0.125
— 257°.24	+ 0.144

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

OF THE UNIVERSITY OF
9 NOV 191

N°. 128.

H. KAMERLINGH ONNES and **C. A. CROMMELIN**. — Isotherms of monatomic substances and of their binary mixtures. XIII. The empirical reduced equation of state for argon.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, **29 Juni 1912**, p. 256—263).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and C. A. CROMMELIN. *Isotherms of monatomic substances and of their binary mixtures.* XIII. *The empirical reduced equation of state for argon.*

In a previous paper [1]) we indicated the desirability of obtaining from the mean reduced empirical equation of state for a number of normal substances which we have called VII. 1. [2]), a mean reduced empirical group-equation applicable to the monatomic substances. As a first step in that direction we now give a special reduced empirical equation for argon which we shall call VII. A. 3. and which embraces data obtained from observations made in both vapour and gaseous states [3]).

In previous communications similar special equations have been published, viz. one for carbon dioxide [4]) in gas, vapour and liquid states, and one for hydrogen [5]) which embraced all available observations on the gaseous state. The important part as convenient summaries of all available experimental data played by such special equations in all sorts of thermodynamical calculations concerning the particular substance within the limited range through which the equation holds makes it essential to obtain the best possible agreement between the equation and the results yielded by experiment. As the form VII. 1. was chosen for this equation with a view to its relationship to other investigations concerning the equation of state, it was therefore fortunate that, for the comparatively small region of temperature covered by the argon observations, there were still the same number of coefficients available for the equation as had been found required to give good average agreement over the whole region covered by the equation of state for various different substances.

In the paper [3]) which contained the isotherm determinations for argon we have already given preliminary values for the individual virial coefficients A_A, B_A, etc. of the equation

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[1]) Comm. N^0. 120*a*.

[2]) Suppl. N^0. 19 pag. 18.

[3]) Comm. N^0. 118*b* and C. A. CROMMELIN, Theses for the doctorate, Leiden, 1910.

[4]) Arch. néerl. (2). 6. 874. 1901, Comm. N^0. 74.

[5]) Comm. N^0. 109*a*.

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v_A^2} + \frac{D_A}{v_A^4} + \frac{E_A}{v_A^6} + \frac{F_A}{v_A^8}$$

as directly calculated from the observations for each individual isotherm.

The reduced virial coefficients $\mathfrak{B}$, $\mathfrak{C}$, etc. have now been calculated from the virial coefficients B_A, C_A etc. as functions of the reduced temperature $\mathfrak{t}$, which comes to the same as the evaluation of the constants in the equations

$$\left.\begin{aligned} \mathfrak{B} &= \mathfrak{b}_1\mathfrak{t} + \mathfrak{b}_2 + \frac{\mathfrak{b}_3}{\mathfrak{t}} + \frac{\mathfrak{b}_4}{\mathfrak{t}^3} + \frac{\mathfrak{b}_5}{\mathfrak{t}^5} \\ \mathfrak{C} &= \mathfrak{c}_1\mathfrak{t} + \mathfrak{c}_2 + \frac{\mathfrak{c}_3}{\mathfrak{t}} + \frac{\mathfrak{c}_4}{\mathfrak{t}^3} + \frac{\mathfrak{c}_5}{\mathfrak{t}^5} \end{aligned}\right\} \text{etc.} \quad {}^{1)} \quad \ldots\ldots \quad (I)$$

By this the coefficients are adjusted to the observations with respect to both temperature and density.

We may here give a short résumé of the manner in which these calculations were carried out.

As in the present instance the final terms of the polynomial $pv_A = A_A + \frac{B_A}{v_A} +$ etc. exert but a slight influence and therefore can be calculated only approximately from the observations, it was best to begin with the adjustment of those terms. The fairly great changes which these terms as a rule undergo have but a slight influence upon the values of the initial coefficients, while, on the other hand, small changes made in the initial coefficients in the process of adjustment occasion appreciable alterations in the coefficients of the final terms, and so the adjustment of the values of the final coefficients would become more difficult than it is as a rule at small densities.

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[1]) Comm. N°. 71 and Arch. néerl. (2) 6. 874. 1901, Comm. N°. 74.

As can be seen a 5th term has been added to the equations there given. For the formulae connecting B_A and $\mathfrak{B}$, C_A and $\mathfrak{C}$, etc., reference may be made to the former paper. In the present paper we shall use chiefly the reduced virial coefficients which are to be preferred for the adjustment of the values of the coefficients.

In the case of argon the coefficients $\mathfrak{E}$ and $\mathfrak{F}$ need not be taken into account, for their values have been adopted from VII. 1. ¹) and consequently they have already been adjusted to the observations Our calculations therefore began with the adjustment of $\mathfrak{D}$ which, as a glance at the values of D_A already published ²) will clearly show, had to be done in a somewhat arbitrary manner. Some of these D_A's have been taken from VII. 1. The values of D_A at the lower temperatures, which were very irregular, were now plotted, while for $\mathfrak{t} = 6$ the D_A value from VII. 1. was included In this way values of D_A or $\mathfrak{D}$ were graphically smoothed, and then the deviations of these smoothed values from VII. 1. were represented as functions of the reduced temperature by a linear equation

$$\Delta \mathfrak{D} = \Delta \mathfrak{d}_1 \mathfrak{t} + \Delta \mathfrak{d}_2$$

(in which

$$\begin{aligned} \Delta \mathfrak{D} &= \mathfrak{D}_a - \mathfrak{D}_{\mathrm{VII.1.}} \\ \Delta \mathfrak{d}_1 &= \mathfrak{d}_{1.a} - \mathfrak{d}_{1.\mathrm{VII.1.}} \\ \Delta \mathfrak{d}_2 &= \mathfrak{d}_{2.a} - \mathfrak{d}_{2.\mathrm{VII.1.}}) \end{aligned}$$

In this way $\mathfrak{d}_{1.a}$ and $\mathfrak{d}_{2.a}$ were calculated as functions of the reduced temperature, while $\mathfrak{d}_{3.a}$, $\mathfrak{d}_{4.a}$ and $\mathfrak{d}_{5.a}$ were taken from VII. 1.

The values of $\mathfrak{D}$ adjusted in this way were then converted into D_A and were used in the first place to get an idea of the magnitude of the corrections to be applied to the values of $\mathfrak{B}$ and $\mathfrak{C}$ so as to give the best possible agreement with the observations. When this was done we could then proceed to the proper adjustment of the values of B_A and C_A, or rather of $\mathfrak{B}$ and $\mathfrak{C}$ according to the formulae (I).

As can be seen from what follows, this process yielded values of the coefficients which, especially as regards the $\mathfrak{B}$ coefficient, did not differ much from those of VII. 1. while, at the same time, a comparison with the experimental data of the reduced equation of state thus obtained gave thoroughly satisfactory results. The results of all these calculations viz. the coefficients $\mathfrak{b}_1$, $\mathfrak{b}_2$, $\mathfrak{b}_3$, $\mathfrak{b}_4$, $\mathfrak{b}_5$, $\mathfrak{c}_1$, $\mathfrak{c}_2$, etc., of the equation VII.A.3., the virial coefficients

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1) Suppl. N°. 19 pg. 18.

2) Comm. N°. 118*b*.

obtained from these, and finally, the comparison of VII. A. 3. with the experimental data are given in the following tables.

The figures italicised in the tables are those which have been taken from VII. 1.

TABLE I. Coefficients of the equation VII. A. 3.

	1	2	3	4	5
$\mathfrak{b} \times 10^8$	+ 137.193	— 146.732	— 505.734	+ 94.358	— 17.8488
$\mathfrak{c} \times 10^{11}$	+ 97.9740	— 528.608	+ 836.166	— 315.182	+ 77.4006
$\mathfrak{d} \times 10^{18}$	+ 236.30	+ 421.825	— *903.004*	+ *367.7055*	— *178.5625*
$\mathfrak{e} \times 10^{25}$	— *1588.948*	+ *5725.652*	— *4331.720*	+ *864.610*	+ *40.449*
$\mathfrak{f} \times 10^{32}$	+ *1685.000*	— *6477.876*	+ *6019.629*	— *1512.028*	+ *144.537*

TABLE II. Virial coefficients of equation VII. A. 3.

ϑ	A_A	$B_A \times 10^3$	$C_A \times 10^6$	$D_A \times 10^{12}$	$E_A \times 10^{18}$	$F_A \times 10^{24}$
+ 20.39	+ 1.07545	— 0.60178	+ 0.76768	+ 6.78079	+ *7.6045*	— *4.35430*
0.00	+ 1.00074	— 0.76763	+ 0.91203	+ 5.93894	+ *8.7321*	— *4.98937*
— 57.72	+ 0.78922	— 1.30257	+ 1.50907	+ 3.28679	+ *10.5255*	— *5.02409*
— 87.05	+ 0.68174	— 1.62411	+ 1.92013	+ 1.18908	+ *10.5566*	— *3.93044*
— 102.51	+ 0.62511	— 1.81201	+ 2.16108	+ 0.72267	+ *10.4013*	— *3.10842*
— 109.88	+ 0.59810	— 1.90692	+ 2.28115	+ 0.20350	+ *10.3251*	— *2.69045*
— 113.80	+ 0.58372	— 1.95896	+ 2.34653	— 0.09396	+ *10.2947*	— *2.47655*
— 115.86	+ 0.57617	— 1.98675	+ 2.38134	— 0.25708	+ *10.2837*	— *2.35600*
— 116.62	+ 0.57340	— 1.99711	+ 2.39431	— 0.31873	+ *10.2806*	— *2.31432*
— 119.20	+ 0.56393	— 2.03255	+ 2.43867	— 0.53362	+ *10.2759*	— *2.17669*
— 120.24	+ 0.56012	— 2.04701	+ 2.45677	— 0.62312	+ *10.2764*	— *2.12239*
— 121.21	+ 0.55658	— 2.06056	+ 2.47376	— 0.70808	+ *10.2783*	— *2.07246*
— 130.38	+ 0.52296	— 2.19283	+ 2.64178	— 2.10863	+ *10.3966*	— *1.66293*
— 139.62	+ 0.48909	— 2.33484	+ 2.83477	— 2.41358	+ *10.8045*	— *1.42979*
— 149.60	+ 0.45252	— 2.50118	+ 3.10431	— 2.78849	+ *11.8440*	— *1.53961*

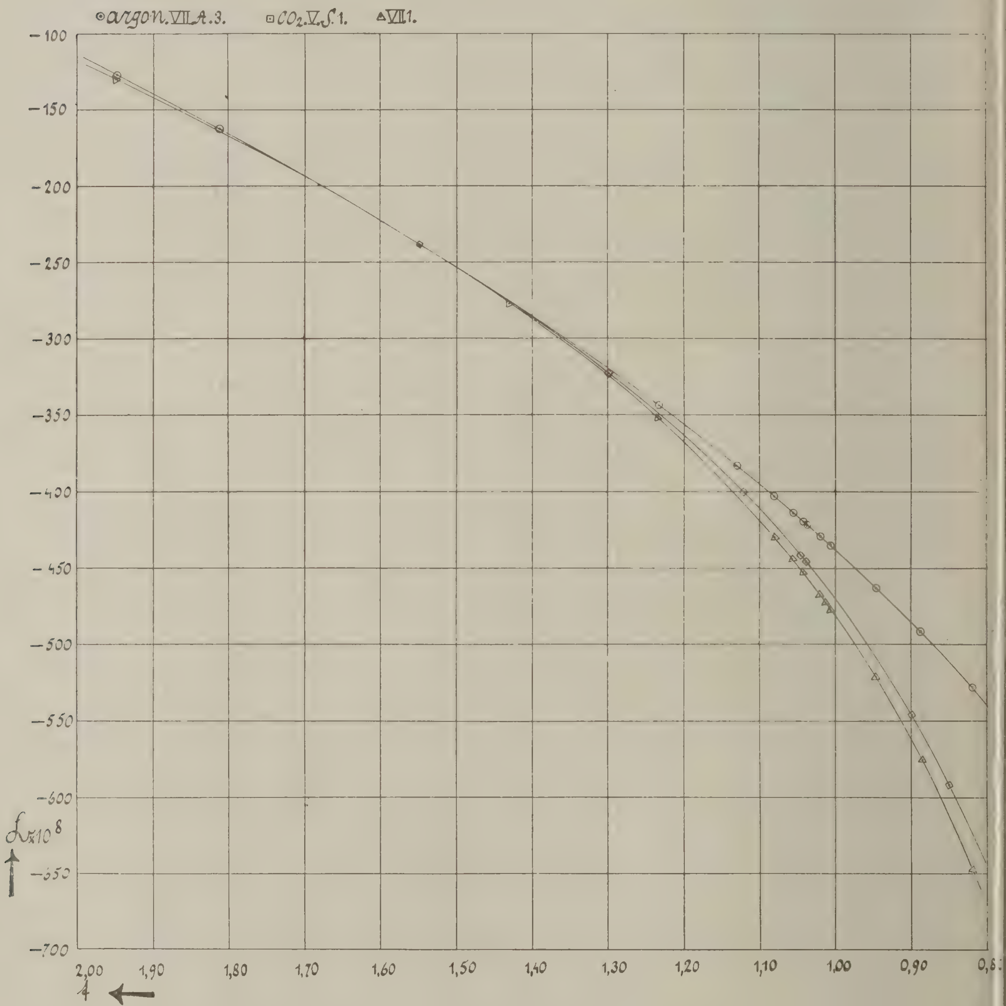
Erratum Communication N^0. 128.

p. 6 line 12 from the bottom: for „1,18908" read: „1,69487".

TABLE III. Comparison of equation VII. A. 3 with observation.

d_A	O—C in %	d_A	O—C in %	d_A	O—C in %	d_A	O—C in %
+ 20°.39		0°.00		— 57°.72		— 87°.05	
20.499	— 0.07	20.877	+ 0.05	23.509	+ 0.11	25 152	+ 0.17
25.759	+ 0.01	26.581	— 0.02	[28 575	— 0.16]	34.467	+ 0.02
32.590	+ 0 14	32.302	+ 0.05	33.793	— 0 05	55.822	— 0.10
35.330	— 0.09	37.782	— 0.06	48.116	0.00	71.444	— 0.06
35.759	— 0.13	51.840	— 0.15	64.948	+ 0.06	94.625	— 0.14
47.319	— 0.04	65.325	— 0.21	90.695	+ 0.11	119.84	+ 0.19
59.134	+ 0.07						
59.250	— 0.06						
— 102°.51		— 109°.88		— 113°.80		— 115°.86	
25.571	+ 0.19	26.242	+ 0.14	67.078	— 0.16	69.947	— 0 23
35.077	0.00	34.807	+ 0.26	88.889	— 0.13	91.308	— 0.18
[47.893	+ 0.47]	65.142	— 0.54	106.68	— 0.34	108 02	— 0.35
[53.752	+ 0.48]	66.530	— 0.29	129.17	— 0.25	131.51	— 0.38
62.240	— 0.05	87.176	+ 0.01	152.71	— 0.14	155.12	— 0.27
[69.954	+ 0.50]	102.76	— 0.20	155.40	— 0.07	179.94	— 0 06
84.002	— 0.08	125.56	— 0.09	182.13	+ 0.37	[183.35	+ 2.40]
95 802	— 0 17	148.32	+ 0.03	184.82	+ 0.27	235.47	+ 1.16
115.88	— 0.17	152.79	— 0.26	212.99	+ 1.02	319.52	+ 0.20
135.65	— 0.01	180.84	+ 0.37				
158.01	+ 0.13						
— 116°.62		— 119°.20		— 120°.24		— 121°.21	
26.480	+ 0.25	26.871	+ 0.24	72.627	— 0.04	27.326	+ 0 24
34.939	— 0 01	34.965	+ 0.24	82.816	+ 0.10	35 283	+ 0.25
68.630	— 0.13	[70.314	— 0 25]	99.246	+ 0.03	71.459	— 0.10
90.563	— 0.21	70 481	— 0.66	118 51	— 0.10	85.580	— 0.05
110.19	— 0 46	70 580	— 0.56	136.31	— 0.02	100.33	— 0.03
133.69	— 0 39	83.257	— 0 63	165 79	— 0.09	[123.85	— 0.19]
159.71	— 0.25	96.834	— 0.31	206.57	+ 0.82	148.95	— 0.10
161.75	— 0.35	98.863	— 0.83	280.25	+ 3.22	170.05	— 0.16
[186.15	+ 0.13]	124.97	— 1.10	338.95	+ 0.89	234.13	+ 1.73
210.02	+ 0.64	[143.71	— 0.44]			333.75	+ 1.93
[260.61	+ 1.74]	156 36	— 1.07				
331.29	— 0.46	[172.25	+ 0.07]				
		222.69	— 0.04				
		275 02	+ 1.11				
		336.89	— 1.72				
— 130°.38		— 139°.62		— 149°.60			
27.394	+ 0.30	28.122	+ 0.12	29.183	— 0.03		
[31.583	— 0.44]	35.573	— 0.10	34.646	— 0.14		
34.726	+ 0.24						
55.807	+ 0.20						
65.125	+ 0.14						
77.821	+ 0.77						
[101.71	— 0.81]						

The accompanying diagrams exhibit the reduced coefficients $\mathfrak{B}$ an $\mathfrak{C}$ das functions of the reduced temperature $\mathfrak{t}$ within the region of observation for argon, that is, from $\mathfrak{t} = 2$, to $\mathfrak{t} = 0.8$. The curves drawn through the circles refer to the special argon equation VII. A. 3, those through the triangles to the mean reduced equation VII. 1. and those through the squares to the special equation for carbon dioxide, V. s. 1. [1]



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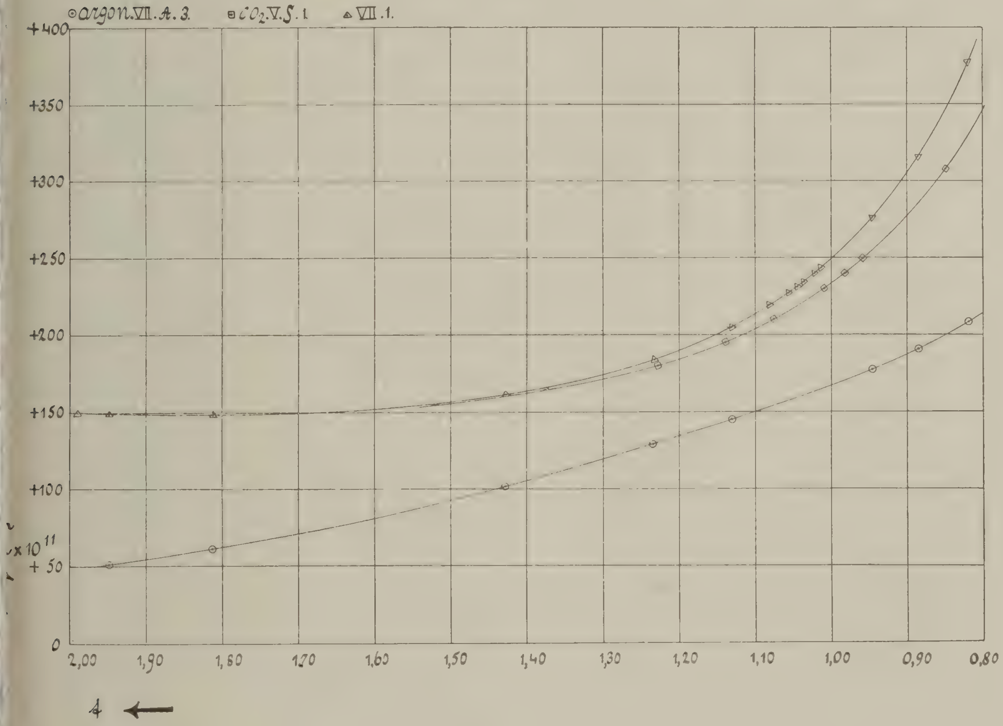
[1] Arch. Neérl. (2), 5, p 874. 1901. Comm. N°. 74.

As the experimental data at present employed are very limited in scope we must, in the meantime, be somewhat chary of drawing conclusions as to the mutual actions of molecules when they come within each other's immediate neighbourhood from a comparison of VII. A. 3. with the equations for the other substances shown in our diagrams. In the case of the 𝔅 coefficient the absence of data at small values of 𝔱 is specially felt[1], while as far as ℭ and the special argon equation are concerned it is the absence of data towards the side of high densities. Equation VII. A. 3 can, therefore, be regarded only as a first step towards the formation of *the* empirical equation of state for argon.



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[1] We hope to be able to publish shortly some experimental results to supply this deficiency.

We may still take it, however, that we have advanced a step since our previous papers 1). It was there found that deviations of the isotherms in the gas state were systematically connected with deviations of the diameter and of the vapour pressure curves (with which the deviations of the latent heat of vaporization etc, are connected by thermodynamical formulae), while in the present case a much simpler survey is obtained of the deviations of the isotherms at densities at which the virial coefficient D need not be taken into account. These are shown in the two curves for $\mathfrak{B}$ and $\mathfrak{C}$, which therefore play pretty much the same part in this particular region as the boundary curve for equilibrium between liquid and vapour. And it is again striking how the various substances arrange themselves as far as these deviations are concerned according to the more or less complicated structure of their molecules. The curves for VII 1 in the region of reduced temperature to which the diagrams refer are obtained chiefly from isopentane and ether, substances which have very complex molecules; after these come, in the order given, carbon dioxide, with an undoubtedly less complex molecule, and finally argon. Clearly, just as was the case with the deviations which were encountered in a previous paper 2), one must look for the explanation of this in a real or apparent compressibility which diminishes in magnitude as the molecule becomes less complex in shape or structure, or in a characteristic behaviour of the attraction potential determined by this peculiarity.

We hope to present further communications shortly giving results of calculations of various thermodynamical quantities which may be made from the equation now given within the limited region for which it holds.

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1) Comm. N^0. 120*b* and N^0. 121*b*.

2) Comm. N^0. 121*b*.

OF THE
VERSITY THE

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 129 a.

H. KAMERLINGH ONNES and **BENGT BECKMAN**. — On the HALL effect and the change in the resistance in a magnetic field at low temperatures. I. Measurements on the HALL effect and the change in the resistance of metals and alloys in a magnetic field at the boiling point of hydrogen and at lower temperatures.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **29 Juni 1912**, p. 263—275).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and BENGT BECKMAN. — *On the* HALL *effect and the change in the resistance in a magnetic field at low temperatures.* I. *Measurements on the* HALL *effect and the change in the resistance of metals and alloys in a magnetic field at the boiling point of hydrogen and at lower temperatures.*

§ 1. *Introduction.* An investigation of the HALL effect and of the change of resistance produced by a magnetic field was carried out by VAN EVERDINGEN at Leiden some time ago down to liquid air temperatures [1]), but the fundamental importance of these phenomena in the theory of electrical conduction has long made it desirable to extend this investigation to the much lower temperatures which have been freely available since the successful development of methods of obtaining accurate series of observations at liquid hydrogen temperatures. The problem, however, has been forced aside by other researches which could not be delayed, until the study of it and of allied problems for various metals at the lowest possible temperatures has been rendered essential to the further development of the theory of electrons by the discovery of the fact that the resistance of pure mercury disappears at liquid helium temperatures. We have therefore been occupied for some time with various aspects of the investigation of these problems at hydrogen temperatures, and, while we propose to continue this investigation systematically and, if possible, to make some measurements on the more important points at those temperatures which are obtainable with liquid helium, we give in the present paper some results which have already been obtained, and which may be considered to be themselves of some importance.

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[1]) The results for bismuth (and antimony) given in the dissertations of LEBRET (Leiden 1895) and VAN EVERDINGEN (Leiden 1897) and in Communications Nos. 19, 26, 37, 40, 53, 58, 61 have been confirmed by BLAKE, Ann. d. Physik. **28**, 449, 1909 and LOWNDS, Ann. d. Physik **9**, 677, 1902. LOWNDS investigated rods cut in different directions from bismuth crystals, and extended his investigation for one direction down to liquid air temperatures. He found that with the crystalline axis perpendicular to the field the HALL coefficient is negative at higher temperatures, while as the temperature is lowered it vanishes and then becomes positive.

The investigation has been extended by one of us (B. BECKMAN) with the same experimental material to temperatures obtainable with liquid ethylene, liquid oxygen and liquid nitrogen, and these results will be discussed in a later paper.

We wish to record our heartiest thanks to Mrs. A. BECKMAN for her assistance in the course of the measurements.

I. *Bismuth.*

§ 2. *Change in the resistance of a wire of electrolytic bismuth.* This part of the investigation was made with a wire of electrolytic bismuth provided by HARTMANN and BRAUN 0.3 mm. thick, and identically the same as that used by KAMERLINGH ONNES and CLAY in their determination of the change of resistance (Comm. N^{0}. 99). The KOHLRAUSCH method of overlapping shunts was used. At ordinary temperature and at the boiling point of hydrogen the main current was 4 milliamps, but at — 259° C. it had to be reduced to 0.1 to 0.2 milliamps on account of the effect of heating upon the resistance. In the following Table w' represents the value of the resistance in ohms in a magnetic field of strength H, w_T is the resistance with no field on, and w_0 is the resistance at 0° C. with no field.

We may notice that we have not obtained the maximum in the isopedals observed by BLAKE. It will be seen from the forthcoming paper on the change of resistance with magnetic field at liquid air temperatures that BLAKE's bismuth wires which showed the maximum exhibited a smaller change in the resistance than ours and were therefore probably not so pure. It is possible that as the purity increases the maximum in the isopedals is displaced towards the lower temperatures.

TABLE I.

Resistance of $Bi_{d\,\mathrm{I}}$ as a function of the temperature and of the field strength.

H Gauss	$T = 290°$		$T = 20°.3$		$T = 15°$	
	w'	$\frac{w'}{w_0}$	w'	$\frac{w'}{w_0}$	w'	$\frac{w'}{w_0}$
0	2.570	1.057	0.588	0.242	0.526	0.216
2760	2.770	1.140	11.5	4.73	—	—
3850	—	—	—	—	19.9	8.185
5540	3.110	1.280	32.8	13.50	34.9	14.35
7370	3.473	1.388	54.7	22.50	55.9	23.00
9200	3.635	1.495	76.7	31.55	80.8	33.25
11850	4.002	1.646	113.2	46.55	116.4	47.90
13600	4.248	1.746	141.5	58.20	143.1	58.85
15670	4.540	1.868	172	70.75	175.6	72.25
17080			196.5	80.85	199.3	82.00

The general character of the isotherms is also conserved at hydrogen temperatures; the field at which the resistance begins to increase practically proportionally to the field itself is about 12000 gauss just as at liquid air temperatures The gradual transformation from the change at small fields to the practically linear change in strong fields takes place in the same way at each temperature.

§ 3. *The* HALL *effect and the increase of resistance for plates of compressed electrolytic bismuth.*

Experimental method.

The method adopted was that developed and applied by LEBRET and VAN EVERDINGEN in their dissertations (see Suppl. N⁰. 2); in it all disturbing influences are eliminated. A diagram is given in Plate 3 of the Supplement quoted, and for all matters concerning the arrangements for measuring we may refer to Chapter I of that paper. Circular plates were used to which were soldered with WOOD's alloy the primary and HALL electrodes as well as two auxiliary electrodes (placed on the diameter in the direction of the main current). All were point electrodes[1]).

Choosing our notation to correspond with that of the Supplement quoted let us write e for the potential difference between the HALL electrodes, I for the main current and d for the thickness of the plate. The HALL constant R is given by

$$R = \frac{ed}{HI}.$$

Let us also write R_s for the resistance of the secondary circuit outside the plate, r for the resistance of the shunt of the compensating circuit, q for a constant determined by the differential galvanometer employed, and R_d for the resistance determined by

$$\frac{1}{R_d} = \frac{1}{2}\left(\frac{1}{R_A} + \frac{1}{R_B}\right)$$

in which R_A and R_B are magnitudes obtained from the resistances of the compensating circuit with reversal of the main current when the field commutator stands in each experiment in the positions A and B respectively; we then obtain

$$R = rdq\,\frac{R_s}{HR_d}.$$

The change in the resistance was also measured as well as the HALL effect.

At ordinary temperature the bismuth plates showed no asymmetry in the HALL effect but they showed it very clearly and sometimes very strongly at hydrogen temperatures, giving considerable differences between R_A and R_B. In the following tables twice the asymmetry is given alongside the mean HALL-constant; for the method of evaluating the asymmetry we may again refer to Chapter I of Suppl. N⁰. 2. All quantities except w are expressed in C. G. S.

The current in the main circuit was $I = 0.15$ amp. A WIEDEMANN galvanometer was used. The bath of liquid gas in the magnetic field was obtained in a silvered vacuum vessel by the method of Comm. N⁰. 114.

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[1]) VAN EVERDINGEN has solved the problem theoretically for point electrodes with circular plates.

§ 4. *Results of the measurements.*

Bi_{pI}, Bi_{pII}, Bi_{pIII}, represent three plates of 10 mm. diameter prepared from the same HARTMANN and BRAUN electrolytic bismuth. Bi_{pI} was compressed from a thin rod in a steel mould. Bi_{pII} and Bi_{pIII} were prepared by first grinding the bismuth to a fine powder in an agate mortar and then compressing in the same mould as Bi_{pI}. In the preparation of Bi_{pIII}, which was otherwise the same as that of Bi_{pII}, the grinding operation took place in an atmosphere of carbon dioxide.

TABLE II.

The HALL constant, asymmetry and resistance change for Bi_{pI}.

H	$T = 289°$				$T = 20°.3$			
	RH	2 × Asym.	$-R$	$\left[\frac{w'}{w}\right]_T$	RH	2 × Asym.	$-R$	$\left[\frac{w'}{w}\right]_T$
2060	13.9×10^3	0.4×10^3	6.75	1.06	91.4×10^3	39.6×10^3	44.35	10.1
3450	20.9	0.2	6.06	1.12	166.5	48	48.25	21.7
5660	29.1	1.1	5.14	1.21	308	54	54.40	39.3
7160	33.2	0	4.64	1.29	385.5	114.5	53.90	52.0
9880	40.3	1.8	4.08	1.45	563	199	57.00	78.2
11090	42.6	2.3	3.84	1.50	640	243	57.70	89.5
0	$w_T = 0.00209\ \Omega$				$w_T = 0.00044\ \Omega$ $\frac{w_{20°\mathrm{K}}}{w_{289°\mathrm{K}}} = 0.22$			

With no field the ratio of the resistance of Bi_{pI} at hydrogen temperature to that at ordinary temperature is almost the same as the same ratio for the bismuth wire Bi_{dI}; but in a magnetic field the ratio of the resistance at hydrogen temperature to the zero resistance is less for the disc than for the wire Bi_{dI}, thus

$$\text{for } H = 11090 \text{ at } T = 20°.3 \qquad \overset{\text{disc}}{\frac{w'}{w_0}} = 19.7 \quad \overset{\text{wire}}{\frac{w'}{w_0}} = 42.$$

TABLE III. HALL constant, asymmetry and change of resistance for Bi_{pII}.

H	$T = 289°$				$T = 20°.3$				$T = 14°.6$			
	RH	$2 \times$ Asym.	$-R$	$\left[\frac{w'}{w}\right]_T$	RH	$2 \times$ Asym.	$-R$	$\left[\frac{w'}{w}\right]_T$	RH	$2 \times$ Asym	$-R$	$\left[\frac{w'}{w}\right]_T$
2060	18.7×10^3	0.2×10^3	9.08	1.023	152.5×10^3	24×10^3	74.1	1.71	167.5×10^3	3×10^3	81.3	1.788
3450	28.2	0.2	8.17	1.057	230	29	66.7	2.31	262	5.5	75.9	2.42
5660	39.85	0.4	7.05	1.108	349.7	37.5	61.8	3.28	—	—	—	—
7160	46.1	0.3	6.44	1.148	431.2	50	60.3	3.93	509	14	71.1	4.14
8520	52.15	0.8	6.12	1.186	503	76	59.0	4.58	—	—	—	—
9880	55.9	0.2	5.66	1.222	583	79	59.0	5.21	687	20	69.5	5.47
11090	59.95	0.8	5.41	1.26	647.5	91	58.4	5.76	755	11	68.1	6.07
12090	62.8	1.4	5.19	1.287	700	100	57.9	6.25	818	20	67.7	6.51
0	$w_{289} = 0.00389\ \Omega$				$w_{20} = 0.00487\ \Omega$							

In the case of Bi_{pII} both the negative temperature coefficient and the smallness of the change of resistance with magnetic field indicate the presence of impurity.

TABLE IV.

The HALL constant, asymmetry and resistance change for $Bi_{p\,III}$.

H	$T = 20°$.			
	RH	$-R$	Asym.	$\left[\frac{w'}{w}\right]_T$
2850	247×10^3	86.6	137×10^3	2.16
4700	426	90.7	210	2.91
6675	624	93.5	280	3.67
8275	814	98.5	346	4.44
10160	1007	99.2	400	5.12
11100	1105	99.4	425	5.49
12220	1216	99.5	460	5.87

With the disc Bi_{pIII} measurements were made only at hydrogen temperatures, but we give the results here as, just as with Bi_{pI}, R increases with H, and approaches a limiting value, approximately 100; this is the highest HALL coefficient yet obtained for bismuth.

All the coefficients we have obtained for bismuth plates are *negative*. Circumstances which give rise to positive ¹) coefficients occur only in certain positions of the crystalline axis and therefore, since all positions of the axis occur at random, they are obscured by those which give rise to negative coefficients.

II. *Other Metals.*

§ 5. *Experimental method.* This was just the same as for bismuth. A THOMSON differential galvanometer was used for observing the HALL

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¹) Here total coefficients are considered, cf. Comm. No. 129c.

effect. Now the contacts were not soldered with Wood's alloy, but with tin.

§ 6. Hall *effect for Gold.* The plate Au_{pI} was prepared from a dutch 10 fl. coin; this was dissolved in aqua regia precipitated by SO_2, melted in a porcelain crucible and rolled between steel rollers. During the last operation and afterwards it was treated with various acids. From the decrease with temperature of the resistance with no magnetic field (see Table V) it is seen that this plate was made of purer gold than that which composed the wire Au_0 of Comm. N⁰. 99, which gave $w_{T=20}/w_{T=273} = 0.045$ and was known to contain 0,03 °/₀ impurity.

d was 0.101 mm., I approximately 1 2 amp, and $R_s = 0.6$ to 0.7 ohms.

We found:

TABLE V.

The Hall effect for Gold Au_{pI}.

H	$T = 290°$.		$T = 20°.3$.		$T = 14°.5$.	
	RH	$R.10^4$	RH	$R.10^4$	RH	$R.10^4$
7730	5.62	7.27	7.57	9.79	7.56	9.78
9500	6.75	7.11	9.32	9.81	9.22	9.71
11080	8.11	7.32	10.91	9.84	11.03	9.96
12220	8.85	7.25	11.98	9.81	12.00	9.82
$w_{T=290} = 202.10^{-6}\ \Omega$			$w_{T=20.3} = 6.7.10^{-6}\ \Omega$			

§ 7. Hall *effect for Silver.* The plate Ag_{pI} was prepared from silver for which we are indebted to the Master of the Royal Mint, Dr. C. Hoitsema. The silver was found to be practically the same as that of the wire Ag_{I} of Comm. N⁰. 99, which had 0.18 °/₀ impurity, and for which $w_{T=20}/w_{T=273} = 0.0089$ (cf. w_T in Table). The thickness of the plate, $d = 0.096$ mm.

Erratum Communication N⁰. 129*a*.

p. 10 line 12 from the top: for 1 2 read 1.2.

TABLE VI.

The HALL effect for Silver $Ag_{\mathrm{p\,I}}$.

H	$T = 290°$ K.		$T = 20°.3$ K.		$T = 14°.5$ K.	
	RH	$R.10^4$	RH	$R.10^4$	RH	$R.10^4$
4940	3.97	8.04	—	—	—	—
7260	5.81	8.01	7.39	10.18	7.22	9.95
9065	7.23	7.98	9.22	10.17	8.98	9.91
10270	8.16	7.95	10.34	10.07	10.12	9.85
w	$173.10^{-6}\ \Omega$		$1.47 \times 10^{-6}\ \Omega$		$0.925 \times 10^{-6}\ \Omega$	
w/w_0	1.065		0.00905		0.0057	

§ 8. HALL *effect for electrolytic Copper.* The electrolytic copper was supplied by FELTEN and GUILLAUME; d was in this case 0.057 mm. We found:

TABLE VII.

The HALL effect for Copper Cu_{pI}.

H	$T = 290°$ K.		$T = 20°$ K.		$T = 14°.5$ K	
	RH	$R.10^4$	RH	$R.10^4$	RH	$R.10^4$
7260	3.59	4.95	4.79	6.60	4.79	6.60
9065	4.42	4.87	6.03	6.65	5.94	6.55
10270	5.08	4.95	6.78	6.60	6.71	6.54
w	$312.10^{-6}\ \Omega$		$2.94.10^{-6}\ \Omega$		$2.83.10^{-6}\ \Omega$	
w/w_0	1.065		0.0103		0.00907	

§ 9. HALL *effect for Palladium.* The plate Pd_{pI} was supplied by HERAEUS; $d = 0.100$ mm. We found:

TABLE VIII.

The Hall effect for Palladium Pd_{pI}.

H	$T = 290°$		$T = 20°.3$		$T = 14°.5$	
	RH	R	RH	R	RH	R
8250	5.61	6.80×10^{-4}	11.42	13.83×10^{-4}	11.54	13.98×10^{-4}
9065	6.04	6.66	—	—	—	—
9360	—	—	12.71	13.58	12.96	13.84
9760	6.64	6.80	—	—	—	—
10270	—	—	14.0	13.63	14.09	13.74
w	$126.2 \times 10^{-5}\,\Omega$		$6.11 \times 10^{-5}\,\Omega$		$5.77 \times 10^{-5}\,\Omega$	
$\frac{w}{w_0}$	1.065		0.0515		0.0485	

The plate was annealed and was kept from contact with the liquid hydrogen in the bath by a coat of celluloid dissolved in amyl acetate. By immersing the same plate unprotected in the bath, so that it absorbed a quantity of hydrogen it was found that the occlusion of hydrogen constantly diminished the Hall coefficient, as is evident from a comparison of the following data with those of Table VIII. It was observed that the change of resistance with temperature diminished at the same time. We found:

at $T = 20°$ K. $R = 12.0 . 10^{-4}$ $w = 5.3 . 10^{-5}$ Ohm.
then „ $T = 290°$ $R = 6.3 . 10^{-4}$ $w = 107. \; 10^{-5}$
and again „ $T = 14°.5$ $R = 9.4 . 10^{-4}$
„ $T = 20°.3$ $R = 10.4 . 10^{-4}$ $w = 6.9 . 10^{-5}$
finally „ $T = 290°$ $w = 109. \; 10^{-5}$

§. 10. *Summary of results dealing with the change in the* Hall *coefficient for various metals.* In the two subsequent Tables we give figures for the change in the Hall coefficient when the temperature sinks to hydrogen temperatures and in the region of liquid hydrogen temperatures; R is the mean value taken from the previous tables at each definite temperature for each substance.

TABLE IX.

The HALL coefficient R at hydrogen temperatures.

T	Au_{pI}	Ag_{pI}	Cu_{pI}	Pd_{pI}
290°	7.24×10^{-4}	8.00×10^{-4}	4.92×10^{-4}	6.75×10^{-4}
20°.3	9.81	10.14	6.62	13.68
14°.5	9.82	9.91	6.56	13.85

TABLE X.

Change of the HALL coefficient $\frac{R_T}{R_{290^\circ \text{K}}}$ on cooling to and in the region of liquid hydrogen temperatures.

T	Au_{pI}	Ag_{pI}	Cu_{pI}	Pd_{pI}
290°	1	1	1	1
20°.3	1.355	1.265	1.345	2.03
14.5	1.355	1.24	1.335	2.05

The change of the HALL coefficient on cooling to the temperature of liquid air $\frac{R_{T=83}}{R_{T=293}}$ has been found by SMITH [1]) to be

1.03 for Au, 1.095 for Ag, and 1.205 for Cu.

It seems to be of great importance that the change in the HALL coefficient for Ag and Au takes place chiefly below —190° C and becomes practically constant again in the region of liquid hydrogen temperatures. This is also seen to be the case for palladium on comparison of the results of experiments by BENGT BECKMAN upon palladium at liquid air temperature, which are not in agreement with those given by SMITH, and which will be published in the forthcoming paper by BENGT BECKMAN. In connection with the different behaviour for copper, for which BECKMAN has already found an increase in liquid air although smaller than that given by SMITH, the question arises if this cannot be accounted for principally by the influence of impurity. Experiments which we have already undertaken upon alloys — in § 12 we give one set of results — will enable us to decide the point.

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[1]) A. W. SMITH, Phys. Review, 30, 1, 1910.

§ 11. *Change of resistance of* Au_{pI}, Pd_{pI}, Cu_{pI}, *in a magnetic field.*

From the measurements with these plates only approximate results can be obtained for this change on account of the smallness of the change in the already very small resistance. In the following table results which were obtained in fields of from 10000 to 11000 gauss are reduced to a standard field of 10 kilogauss.

TABLE XI.

Change of resistance in a magnetic field w'_T / w_T.

H	T	Au	Cu	Pd
10 Kilogauss	20°.3 K	1.017	1.14	1.0015
10 ,,	14°.5		1.10	

While at ordinary temperature the change caused in the resistance by the field is extremely small, at hydrogen temperatures it becomes quite appreciable.

III. *Alloys.*

§ 12. *Gold-Silver.* On account of the usually great influence of admixture upon the HALL effect and upon the magnetic change of resistance it was thought desirable to investigate various kinds of alloys. We are already in a position to communicate details of the behaviour of one *solid solution*, viz. an alloy formed by fusing 2% by volume of silver with gold. The exact analysis we shall publish later, d was here 0.073 mm.

TABLE XII.

The **Hall** effect for a gold alloy.

H	$T = 290°$		$T = 20°.3$		$T = 14°.5$	
	RH	R	RH	R	RH	H
8250	5.70	6.91×10^{-4}	5.60	6.79×10^{-4}	5.44	6.60×10^{-4}
9065	6.31	6 96	—	—	—	—
9360	—	—	6.46	6.90	—	—
9760	6.75	6.91	—	—	6.44	6.60
10270	7.08	6.90	7.01	6.83	6.80	6.62
0	$w = 3.81 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 1.045$		$w = 1.083 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 0.298$		$w = 1.080 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 0.297$	

Here we have

$$\frac{R_{T=20.3}}{R_{T=290}} = 0.985.$$

$$\frac{R_{T=14.5}}{R_{T=290}} = 0.955.$$

The observations show that down to hydrogen temperatures and in that region itself the Hall coefficient decreases slightly; both changes however are so small that they do not exceed the limits of the probable error.

POSTSCRIPT.

IV. *Bismuth crystals.*

§ 13. Hall *effect in bismuth crystals.* We were not very successful with some of our measurements upon the rods cut in various directions from a crystal which had been formerly used by van Everdingen in his researches, and we had therefore meant to postpone the communication of our results until we had obtained a complete series of determinations for various positions of the axis; just as we go to press, however, the important paper by J. Becquerel in the Comptes Rendus for 24th June 1912 reaches us, so that we now publish the result which we had already obtained for the case treated by Lownds; it is given in the following Table.

TABLE XIII.

Hall effect in a Bismuth crystal with the axis perpendicular to the field.

$T = 290°$			$T = 20°.3$		
H	RH	R	H	RH	R
2010	20.0×10^3	-9.95	1850	18.0×10^3	$+9.72$
3740	30.6	-8.18	3700	26.0	$+7.03$
5870	38.6	-6.58	5800	33.6	$+5.79$
8250	42.1	-5.11	8700	43.7	$+5.02$
10270	44.3	-4.31	11080	53.1	$+4.79$

At hydrogen temperatures R is positive and approximates to a constant value; at ordinary temperature it is RH corresponding to negative values of R which approaches a constant value. It is possible that small impurities exert considerable influence upon these changes, and it would therefore be risky to conclude from the fact that the value of R at hydrogen temperature which we have found is not greater than that found by Lownds for one direction in liquid air, that no change of any importance takes place between the latter temperature and that of liquid hydrogen. (The resistance measurements show that Lownds's bismuth plate was freer from impurity than ours).

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 129b.

H. KAMERLINGH ONNES and **E. OOSTERHUIS** — Magnetic Researches VI. On paramagnetism at low temperatures.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **29 Juni 1912**, p. 275—282).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and E. OOSTERHUIS. — *Magnetic Researches.* VI. *On paramagnetism at low temperatures.*

§ 1. *Introduction.* In the present experiments which form a continuation of those discussed by KAMERLINGH ONNES and PERRIER in Comm. N^{os}. 122*a* and 124*a* we have again measured the attraction exerted by a non-homogeneous field upon a long cylinder of the experimental substance. Unless where we state otherwise, the experimental substance was finely powdered and contained in a glass tube just as was done in the researches referred to. In the present experiments, however, we adopted a device which had only been tried a few times in the former series, and, in order to eliminate the effect of the glass, the tube was taken twice as long as the part of it which contained the powder, so that the two halves were the same except that one was evacuated and the other held the powder; the evacuated part was separated from the other by a plug of cotton wool which was placed in our experiments at about the centre of the field of our WEISS electro-magnet We now balanced the attraction by gravity control, and instead of allowing the tube to be drawn down by the attraction of the field and to be raised to its zero position electromagnetically, the tube was now drawn up by the action of the field and was brought down again to its zero position by weights. The modified form of the apparatus allowed much greater forces to be measured without involving any considerable alteration; we shall return to its description when a detailed account will have been given of the apparatus used in the former experiments.

§ 2. *Anhydrous Ferrous-sulphate.* Comm. No. 124*a* stated that it was intended to investigate this substance at temperatures available with liquid nitrogen, so as to fix more definitely the temperature at which χ attains its maximum value, which lay according to the experiments then made between 143° K. and 20° K. While this particular investigation was our principal aim, at the same time we repeated the measurements previously obtained at other temperatures. The salt was dried by heating for some time in vacuo to 280° C. special care being taken with this operation. We obtained the following results: (see table I).

TABLE I.

Anhydrous ferrous-sulphate I.

T	$\chi.10^6$	$\chi.T.10^6$	Limits of H.	Bath.
290°.2 K	67.6	19617	14000—16000	Room atmosphere.
169 6	107.2	18181	14000—17000	Liquid ethylene.
77.3	200.4	15491	14000—17000	Liquid nitrogen.
70.4	215.1	15143		
64.8	227.3	14729		
20.1	402	8080	10000—16000	Liquid hydrogen.
17.8	379	6746		
14.4	335	4824		

If we compare these with the results given in Comm. No. 124*a* for ferrous-sulphate which was practically anhydrous we see that a small admixture of water diminishes the value of χ and that to a

TABLE II.

Ferrous-sulphate III. not quite anhydrous.

T	$\chi.10^6$	Limits of H.	Bath.
289°.5 K	62.1	8000—17000	Room atmosphere.
169.6	95.7	9000—17000	Liquid ethylene.
77.3	169.8	5000—15000	Liquid nitrogen.
70.4	182.0		
64 8	189.8		
20.1	231.4	4000—17000	Liquid hydrogen.
17.8	220.6		
14.4	204.8		

very large extent at hydrogen temperatures. For while the increase in the value of χ brought about by more efficient drying is only a few percent at ordinary temperature, it is as much as 50 % at 20° K. That we must really look in this direction for an explanation of the differences between the numbers given in November 1911 and those now communicated is evident from an experiment in which the quantity of moisture present in the ferrous-sulphate was purposely increased slightly (the quantity of water present being probably a little greater than that of ferrous-sulphate II, by which we designate the specimen used by KAMERLINGH ONNES and PERRIER). For this not quite anhydrous ferrous-sulphate III we found the data given in table II (p. 20).

§ 3. *Deviations from* CURIE's *law.* In previous Communications an attempt was made to establish a law other than CURIE's (which as appears from Table I does not hold for anhydrous ferrous sulphate) to represent empirically the variation of χ with temperature; for this was given the law $\chi \sqrt{T} = const.$ which did quite well indeed represent the various observations then under consideration. The analogy of phenomena exhibited by ferric sulphate, which lead one to believe that that substance exhibits ferromagnetism at low temperatures, suggested to us to express χ^{-1} as a function of the temperature, and we found that the formula $\chi(T + \Delta') = C'$, which has also been used by WEISS and FOËX [1] [2]), was worth trying with positive values of Δ' and C'. As long as we keep above — 208° C. this formula is quite satisfactory for the representation of the deviations from CURIE's law at low temperatures found by KAMERLINGH ONNES and PERRIER

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[1] Starting with the idea of corresponding states for para- and ferro-magnetic substances, we were led to the formula $\chi(T + \Delta') = C'$ by an attempt to determine the absolute temperature Θ of the possible CURIE point with the help of experimental data in the suspected region of the "magnétisme sollicité". We found Θ negative, which brought to our minds the notion of the inverse field by which VOIGT has tried to explain certain peculiarities of the ZEEMAN effect as shown by salts of the rare earths. It was only after we had represented the deviations from CURIE'S law shown by paramagnetic substances at low temperatures by means of this molecular diamagnetic field that we noticed that WEISS and FOËX had in the same way represented the behaviour of γ-iron and the nickel alloys above the CURIE point. WEISS and FOËX show that there is no prima facie cause why the WEISS molecular field could not occur with the opposite sign. It speaks well for the reasonableness of the hypothesis that we should be led to it for entirely different substances and under circumstances in which the quantity $\frac{H}{T}$, fundamental in paramagnetism, is so much greater than in the experiments made by WEISS and FOËX.

[2] After this communication was printed in dutch, we received the dissertation of A. PREUSS, Zürich 1912, in which there is found also a negative molecular field for the alloys of Fe with less than 16 % Co. [Note added in the translation.]

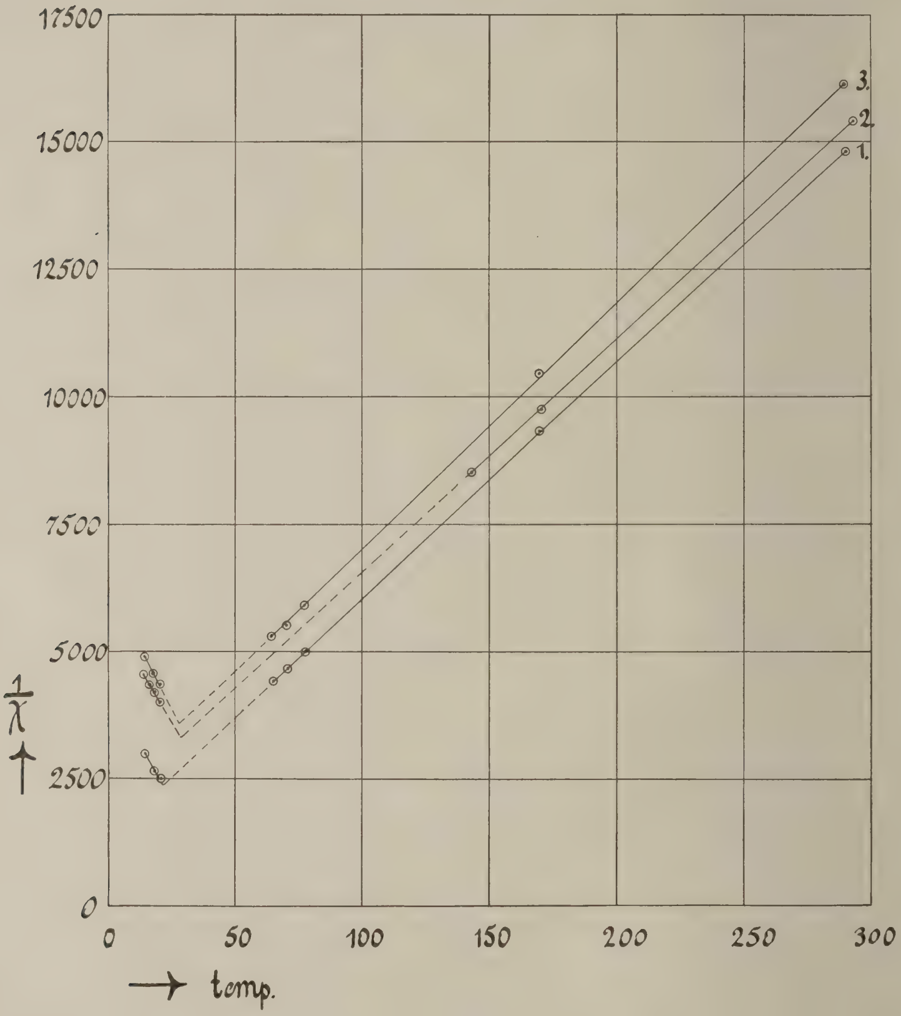

Fig. 1.

and by us up to the present; we shall give several instances of this in § 7. The variation of χ as a function of the temperature can then be expressed for ferrous sulphates of different degrees of dryness by ascribing different values to Δ'. Below the maximum χ^{-1} remains still linear, at least to a first approximation, but the constant, C'', which replaces the CURIE constant in that region, is negative, as is also Δ'', the constant which replaces Δ'.

The results obtained for ferrous sulphates I, II and III are shown graphically in Fig. 1. C' and C'' are seen to be practically equal for the different degrees of dryness, while Δ' (31° for ferrous sulphate I) and Δ'' differ and increase in magnitude with the quantity of moisture present in the salt [1]). The difference between the values of C' and C'' for different degrees of dryness is so small that it practically coincides with the limits of accuracy of the observations. On the present representation the temperature at which χ attains its maximum value is given by the point of intersection of the two lines, which are determined by the constants C' and Δ', in the first disturbed paramagnetic state (we shall designate that state normal in which the CURIE law holds), and by the constants C'' en Δ'' in the second disturbed paramagnetic state. The temperature of the maximum therefore alters with the quantity of moisture contained in the salt. It lies just above the boiling point of hydrogen, so that a new arrangement of the experiment is necessary before the correctness of this deduction can be tested and at the same time an investigation made as to whether the formula given holds good up to the maximum or not. That this is probably so is corroborated by the fact that on cooling ferrous sulphate I down to 20° K. χ would increase continuously until it began to fluctuate about its mean final value, while on cooling ferrous sulphate III χ clearly overstepped its maximum value before the temperature of the bath was reached, just as is to be expected from the diagram.

§ 4. *Anhydrous ferric sulphate down to* —208° C. Anhydrous ferric sulphate was also investigated at the same time as the ferrous sulphate to ascertain any possible influence of the valency of the iron atom, and to see if χ for ferric sulphate also reached a maximum value. Down to the temperatures available with liquid nitrogen and in that temperature region we found perfectly regular behaviour corresponding to what we have termed the first disturbed paramagnetic state. We found:

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[1]) For crystallized ferrous sulphate the line, according to Table II, Comm. N°. 122*a* of KAMERLINGH ONNES and PERRIER, is passing almost through the origin, Δ' being 2° only So interposition of a small number of watermolecules seems to increase Δ' and of a great number to reduce it to a very small value. [Note added in the translation.]

TABLE III.

Anhydrous ferric sulphate I above — 208° C.; $\Delta' = 31$.

T	$\chi \cdot 10^6$	$\chi(T+\Delta')10^6 = C' \cdot 10^6$	Limits of H.	Bath.
289°.8 K	53.3	17100	9000—15000	Room atmosphere.
169 .6	85.6	17170	7000—17000	Liquid ethylene.
77 .4	157.2	17040	14000—17000	Liquid nitrogen.
70 .5	167.3	16980		
64 .9	177.1	16980		

Valency, which plays such an important part in solutions, has here but a very slight influence down to and at nitrogen temperatures; the difference between the molecular susceptibility of anhydrous ferric sulphate and that of ferrous sulphate I is only about 3%.

We may note that Δ' is the same for both anhydrous ferrous and ferric sulphates.

For the behaviour of ferric sulphate at hydrogen temperatures we may refer to § 8.

§ 5. *Manganese chloride.* Manganese chloride was used which had been freed from water as far as possible; it was not possible to make it quite anhydrous. As can be seen from the following table it obeys CURIE's law exactly at temperatures above —208° C.; values are also given for hydrogen temperatures for which the law no longer holds.

TABLE IV.
Manganese chloride I, pulverised, not quite anhydrous.

T	$\chi \cdot 10^6$	$\chi \cdot T \cdot 10^6$	Limits of H.	Bath.
290°.8 K	106.5	30970	6000—17000 G	Room atmosphere.
169 .6	183.4	31100	5000—17000	Liquid ethylene.
77 .4	403	31190	5000—16000	Liquid nitrogen.
70 .5	440	31020	7000—16000	
64 .9	480	31150	5000—16000	
20°.1	1419	28520	5000—16000	Liquid hydrogen.
17 .8	1589	28280	3000—10000	
14 .4	1881	27090	3000—16000	

§ 6. *Gadolinium sulphate.* The observations of KAMERLINGH ONNES and PERRIER were supplemented by the following which further confirm the validity of CURIE's law and the absence of saturation phenomena.

TABLE V.
Crystallised gadolinium sulphate II.

T	$\chi \cdot 10^6$	$\chi \cdot T \cdot 10^6$	Limits of H.	Bath.
293°.1 K	68.9	20190	9000—17000	Room atmosphere.
20 .1	997	20049	5000—15000	Liquid hydrogen.

This result, on account of the large number of magnetons present in gadolinium sulphate and of the resulting large value of the a of LANGEVIN at this low temperature is of importance to LANGEVIN's theory, according to which saturation phenomena are here still outside the limits of experimental accuracy.

§ 7. *Summary of the deviations from* CURIE's *law.* We here append the representation of the experiments of KAMERLINGH

ONNES and PERRIER on dysprosium oxide (Comm. N⁰. 122*a*) by the formula $\varkappa\,(T + \Delta') = C'$.

TABLE VI.

Dysprosium oxide
represented by the formula
$\varkappa\,(T + \Delta') = C'$; $\Delta' = 16$.

T	$\varkappa \,.\, 10^6$	$\varkappa (T + \Delta') . 10^6$.
288°.5 K	229.2	69790
170	374.6	69670
[132.79	445.7	66320]
20.25	1915	69420
17.94	2032	68970
15.95	2173	69430
13.93	2334	69860

With the exception of the measurement made with liquid ethylene boiling under reduced pressure, which is rendered doubtful by the otherwise good agreement between observation and formula, the differences do not exceed the limits of experimental error.

If we collect the various data hitherto given in this paper the following different cases are seen to occur.

Gadolinium sulphate follows CURIE's law over the whole region of low temperatures down to the lowest hydrogen temperature, 14° K, throughout the whole of this region we may call it a *normal* paramagnetic substance.

Over the whole region of low temperatures and down to the lowest hydrogen temperature dysprosium oxide obeys the law $\varkappa\,(T + \Delta') = C'$ with Δ' and C' positive. Over the whole of this region it shows therefore a disturbance of the first kind, which is to be ascribed to the occurrence of a WEISS molecular field of opposite sign.

Down to —208° C., and perhaps lower, manganese chloride is normal. At hydrogen temperatures it deviates in a manner which

Addendum Communication N^0. 129.

p, 26 line 2 from the top: add a note „cf. Comm. N^0. 132*e* § 13”.

may to a first approximation be represented by $\chi(T + \Delta') = C'$, or, in other words, the disturbance throughout this region is of the first kind. Crystallised ferrous sulphate behaves in exactly the same way. (Comm. N⁰. 122*a*).

Both anhydrous ferrous sulphate I and ferrous sulphate not quite anhydrous (see § 3) show a disturbance of the first kind down to — 208° C. and probably to about — 250° C.; at hydrogen temperatures they show a disturbance of the second kind (both Δ'' and C'' negative).

At low temperatures down to — 208° C. anhydrous ferric sulphate exhibits the same disturbance of the first kind as anhydrous ferrous sulphate. At hydrogen temperatures it exhibits the deviations which are discussed in the following section.

§ 8. *Ferric sulphate at hydrogen temperatures.* For the first time in the course of our observations we here found a dependence of the susceptibility upon the magnetic field which leads one to presume the existence at these temperatures of ferromagnetism in a substance which at ordinary temperatures is paramagnetic. We must in the meantime confine ourselves to this general remark. Accurate data giving magnetisation as a function of the field at different temperatures cannot be immediately deduced from the attractive force exerted upon a long cylinder in a non-homogeneous field, as long as χ remains an unknown function of H. The investigation has therefore in the first place been continued with a cylinder of short length (a disc) of ferric sulphate placed in a certain part of the field at which both H and $\frac{\partial H}{\partial x}$ are known.

We must refer to a subsequent paper for the results obtained and for the deductions which may be drawn from them.

COMMUNICATIONS

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 129c.

H. KAMERLINGH ONNES and **BENGT BECKMAN**. — On the HALL effect, and on the change in resistance in a magnetic field at low temperatures. II. The HALL effect and the resistance increase for bismuth in a magnetic field at, and below, the boiling point of hydrogen.

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EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and BENGT BECKMAN. — *On the* HALL *effect, and on the change in resistance in a magnetic field at low temperatures.* II. *The* HALL *effect and the resistance increase for bismuth in a magnetic field at, and below, the boiling point of hydrogen.*

V. *Linear variation in strong fields.*

§ 14 [1]). *Linear variation of the* HALL *effect for bismuth in strong fields.*

a. As was suggested by J. BECQUEREL, the fact that the HALL effect for bismuth in strong fields can be represented by a linear function of the field strength may be regarded as resulting from the composition of the effect from two separate components. One of these is proportional to the field, and was found by us (see Comm. N°. 129*a* § 4) to be always negative for plates of compressed electrolytic bismuth. The second approaches a limiting value, and, with our plates, was found to be constant at hydrogen temperatures, in fields greater than 3 kilogauss.

That is to say, the law of linear dependence upon the field is rigidly obeyed by the first component of BECQUEREL, within the limits of experimental error in fields greater than 3 kilogauss. As an example we give in Table XIV values calculated from

$$RH = a'H + b' \,, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which $a' = 54.3$ and $b' = 42.10^3$

(with both a' and b' in absolute units), and alongside these we put values for $T = 20°.3$ K taken from Table III.

TABLE XIV.
Linear variation of the HALLeffect for Bi_{pII} in strong fields at $T = 20°.3$ K.

H	RH Obs.	RH Calc.
3450	230×10^3	229×10^3
5660	350	352
7160	431	434
8520	503	507
9880	583	582
11090	647.5	647
12090	700	702

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[1]) The sections of this paper are numbered in continuation of those of Comm. No. 129*a*.

The linear form is found to be just as rigidly obeyed in the experiments made by BENGT BECKMAN upon the same experimental material at the temperature of liquid air; for an account of these experiments we may refer to § 3 of the Communication No. 130*a*.

It is noteworthy that, in the case of the second BECQUEREL component, saturation is most easily attained at low temperatures. In this respect this component is analogous to the magnetization of a ferromagnetic substance. The linear dependence of the first component upon the field strength recalls the behaviour of diamagnetic polarisation. In the region of very low temperatures the very rapid variation of a' with the temperature can be represented by a simple empirical formula which was obtained by compounding the data given by BECKMAN for liquid air temperature (see Communication No. 130*a*). From this it was found that

$$a' = a'_0 e^{-\beta' T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

within the temperature region $90° \mathrm{K} \geqq T \geqq 14° \mathrm{K}$. A much more complicated formula would be required to embrace the observations at higher temperatures as well.

On going down to liquid hydrogen temperatures the constant b', the maximum value of the second BECQUEREL component, which is negative at ordinary temperature becomes positive in the case of Bi_{pI} and Bi_{pIII}. BECKMAN's investigations upon the same plates at the temperature of liquid air show that the reversal of the sign must take place below 72° K.

b. With regard to crystals we have already stated in § 13 that, when the crystalline axis is perpendicular to the field, the HALL effect is negative at ordinary temperature, and approaches a limiting value. To this we may now add that with another rod also with its axis perpendicular to the field we found, at ordinary temperature, a maximum at $H = 9500$, and then a decrease ($10^{-3}\ RH$ fell from 37 to 35.4); this leads us to suspect that proceeding to stronger fields then those we employed would have brought to light the same behaviour in the case of the rod quoted in § 13. At hydrogen temperatures the sign of the HALL effect reverses and becomes positive, increasing linearly with the field for fields above 3 kilogauss [1]). From this it appears that in the case of the axis perpendicular to the field, the positive effect must be much weaker at ordinary temperature than the negative, and begins to be appreciable only at very low temperatures. What we have found for the case of the axis perpendicular to the field is analogous to what BECQUEREL obtained with the axis parallel to the field.

With our crystalline rod placed in a definite position the value of the field at which the second component attains saturation at hydrogen temperatures is the same as that at which a plate consisting of crystals of various orientations (for instance, a plate of compressed electrolytic bismuth) reaches saturation. That is to say, on going down to hydrogen temperatures, the saturation field appears to be independent of the orientation.

§ 15. *Linear variation of the increase of resistance of bismuth in strong fields.*

In § 2 we remarked that in strong fields the resistance varied directly as the field. For fields of 12000 gauss upwards we find

$$\frac{w'}{w} = a\,H + b \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

(cf. fig. 1 of the Communication N⁰. 130*a* by BENGT BECKMAN) where the values of a and b vary greatly with peculiarities of the bismuth employed (wire or various plates made from compressed electrolytic bismuth).

It is worth noting that the coefficient a of the linear variation of resistance, and the coefficient a' of the linear variation of the HALL effect can, for temperatures below that of liquid air, be represented by the same functions of the temperature, so that we may write

$$a = a_0\, e^{-\beta T} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

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[1] J. BECQUEREL (C. R. **154**, 1795, 1912) draws attention to the fact that at low temperatures RH becomes very large. The values we here give for hydrogen temperatures make this all the more striking. For Bi_{pII} we obtained $RH = 500.10^3$ for $H = 8500$. With this plate, indeed, at the temperature $T = 90°$ K we get a higher value ($RH = 214.10^3$ for $H = 8500$) than that given by BECQUEREL for his plates. From his data (loc. cit.) we calculate for the temperature of liquid air $RH = 168.10^3$ (or $R = +19.8$) for $H = 8500$.

This is found to be the case when we use the values given by Bengt Beckman for the temperature of liquid air (see sections 2 and 3 of the Communication N⁰. 130*a*, in conjunction with those contained in Tables I, II and III. If we remember that the values of β and β' can differ greatly for the different plates,

(for Bi_{pI} $\beta = 0{,}023$ and $\beta' = 0{,}023$
Bi_{pII} $\beta = 0{,}014$ $\beta' = 0{,}006$
Bi_{pI} $\beta = 0{,}027$)

it is evident that we can as yet give no answer to the question as to whether the values of β and β' are the same or not for pure bismuth, and the agreement in the case of Bi_{pI} can quite well be accidental.

The constant b, which is very small at ordinary temperature, becomes large and negative at hydrogen temperatures.

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COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 130a.

BENGT BECKMAN. — On the HALL effect, and on the change in resistance in a magnetic field at low temperatures. III. Measurements at temperatures between + 17° C. and — 200° C. of the HALL effect, and of the change in the resistance of metals and alloys in a magnetic field.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **28 September 1912**, p. 481—492).

EDUARD IJDO — PRINTER — LEIDEN.

BENGT BECKMAN. — *On the* HALL *effect, and on the change in resistance in a magnetic field at low temperatures.* III. *Measurements at temperatures between + 17° C. and — 200° C. of the* HALL *effect, and of the change in the resistance of metals and alloys in a magnetic field.*

§ 1. *Introduction.* A communication was made by KAMERLINGH ONNES and the present writer to the meeting of June 29th. 1912, of the results of measurements of the HALL effect and of the increase of resistance in a magnetic field made by us at liquid hydrogen temperatures. In the present paper those results are extended to the temperatures which are obtainable with liquid ethylene and liquid oxygen, with the same experimental material and following the same experimental methods. It is of great importance that observations made with any particular substance should be distributed as uniformly as possible over the region of temperature under investigation. The measurements now completed make it possible for the results obtained at liquid hydrogen temperatures to be compared with those of former experimenters, who, without exception, proceed only to liquid air temperatures.

For a description of methods and material we may refer to the above Communication. In order to complete the diagrams of the present paper the results for liquid hydrogen temperatures in the paper quoted are also indicated without making specific mention of the fact on each occasion. The present paper is confined to a discussion of the results obtained with bismuth.

I. *Bismuth.*

§ 2. *Change in the resistance of a wire of electrolytic bismuth.* The resistance of the bismuth wire Bi_{dI} was measured in eight different fields at five different temperatures. $T = 290°$ K, 170° K, 139°.5 K, 90° K and 72° K. These results are given in Table 1. H is the field strength in gauss, w'_T the resistance in ohms in the magnetic field at the absolute temperature T, w_T the resistance without field at that temperature and w, the resistance without field at 0° C.

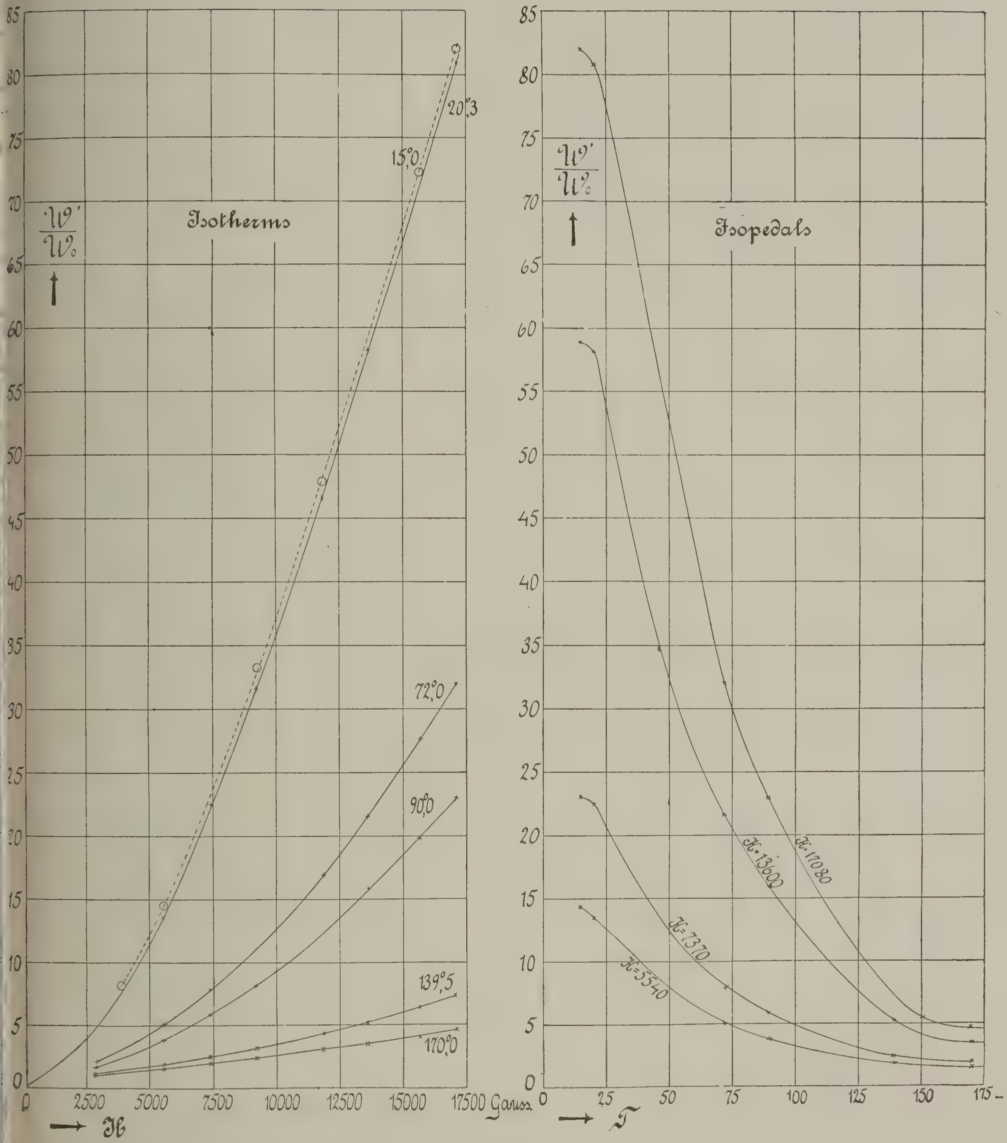
TABLE I.

Resistance of Bi_{dI} as a function of the temperature and of the field.

H in Gauss	$T = 290°$ K.		$T = 170°$ K.		$T = 139°,5$ K.		$T = 90°$ K.		$T = 72°$ K.	
	w'	$\frac{w'}{w_0}$	w'	$\frac{w'}{w_0}$	w'	$\frac{w'}{w_0}$	w'	$\frac{w'}{w_0}$	w'	$\frac{w'}{w_0}$
0	2.570	1.057	1.570	0 646	1.365	0.562	1.075	0.442	0.989	0.407
2760	2 770	1.140	2.366	0.973	2.571	1.058	3.92	1.613	4 68	1 926
5540	3.110	1.280	3.657	1 504	4.414	1 816	9.24	3.80	12.28	5.052
7370	3.473	1.388	4.612	1,897	5.894	2.425	14.20	5.84	19.10	7.86
9200	3.635	1.495	5.613	2 310	7.605	3.128	19.74	8.12	26.6	10.94
11850	4.002	1 646	7.299	3.003	10.56	4 346	29.82	12.27	41.2	16.95
13600	4.248	1.746	8.506	3.500	12 595	5 180	38.60	15.88	52.4	21.6
15670	4.540	1.868	10.204	4.199	15.51	6.380	48 05	19.77	67.2	27.65
17080	—	—	11.412	4.695	17.78	7.316	55.80	22.96	77.8	32.0

Fig. 1. shows the increase of resistance as a function of the field at constant temperature (Isotherms), and fig. 2 the increase of resistance as a function of the temperature under constant field (Isopedals).

In Table II are collected some results obtained by different experimenters for the increase of resistance in a magnetic field. It contains values of $\frac{w_{83°K.}}{w_{273°K.}}$ and $\frac{w'_T}{w_0}$ in a field of 16 kilogauss at the temperature of liquid air.


Isotherms
W'/W₀
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
2500
5000
7500
10000
12500
15000
17500 Gauss
H
20°,3
15°,0
72°,0
90°,0
139°,5
170°,0
Isopedals
W'/W₀
0
25
50
75
100
125
150
175
T
H=17080
H=13600
H=7370
H=5540

Figs. 1 and 2.

TABLE II.

Increase of resistance in a field of 16 kilogauss.

$\frac{w_{83^\circ}}{w_{273^\circ}}$	T	$\frac{w'}{w_0}$	Observer.
0.42—0.44	81° K.	13.3	BLAKE [1]).
—	81°	18.3	BLAKE: 5*b*.
—	83°	23.8	DU BOIS and WILLS [2]).
0.43	90°	20.9	BECKMAN.
	72°	28.7	
0.36	88°	32	DEWAR and FLEMING [3])

The measurements by DEWAR and FLEMING give the largest results for $\frac{w'}{w_0}$ and at the same time the smallest results for $\frac{w_{83^\circ K}}{w_{273^\circ K}}$. They were probably obtained with extremely pure material. BLAKE worked with a large number of different bismuth wires. One of these, labelled 5*b*, gave a larger value for $\frac{w'}{w_0}$ than the others for which he gives a mean value. The wire with which I worked gives exactly this mean value for $\frac{w_{83^\circ K}}{w_{273^\circ K}}$, but a greater value for $\frac{w'}{w_0}$ at the temperature of liquid air. At higher temperatures there is also agreement between BLAKE'S values for the latter ratio and mine.

The maximum in the isopedals found by BLAKE to lie at 36600 gauss at the temperature $T = 99^\circ$ K, and which, for lower temperatures, ought to be found at lower fields, was not observed in the present experiments.

In the weaker fields the isotherms are convex towards the axis of abscissae; from 12 kilogauss upwards they become straight. For $H > 12000$ the relationship

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[1]) P. C BLAKE: Ann. d. Physik. **28**, 449, 1909

[2]) H. DU BOIS and A. P. WILLS: Verh. d. Deutsch. Phys. Ges. **1**, 169, 1899.

[3]) J. DEWAR and J. A FLEMING: Proc. Roy. Soc. **60**, 72, 1896 and 425, 1897.

$$\frac{w'}{w} = aH + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

holds, where a and b are constants, while, at lower temperatures

$$a = a_0 \, e^{-\beta T}$$

to a first approximation. The following Table shows to what degree of approximation this relationship holds.

TABLE III.

a for Bi_{dI}

T	$a_{\text{Obs.}}$	$a_{\text{Calc.}}$
170° K.	1.94	1.95
139°.5	4.2	4.5
90°	18.3	17.1
72°	29.7	27.9
20°	117.5	114
15°	121	131

Even at the boiling point of oxygen b is already clearly negative (— 26.5). As the temperature falls the absolute value of b increases rapidly, and at hydrogen temperatures it reaches the value — 110.

§ 3. *The* HALL *effect and the increase of resistance of plates of compressed electrolytic bismuth.* Tables IV and V contain the results of measurements made at ordinary temperature and at two liquid oxygen temperatures with the plates Bi_{pI} and Bi_{pII}. R is the HALL coefficient in $C. G. S.$ units, D is the asymmetry and Q is the quantity $\dfrac{D}{\dfrac{w'}{w} - 1}$.

TABLE IV.

HALL effect, asymmetry and resistance change for Bi_{pI}.

H	$T = 289°$ K.				$T = 90°$ K.					$T = 74°,5$ K				
	RH	D	$-R$	$\left[\frac{w'}{w}\right]_T$	RH	D	$-R$	Q	$\left[\frac{w'}{w}\right]_T$	RH	D	$-R$	Q	$\left[\frac{w'}{w}\right]_T$
2060	13.9×10^3	0.2×10^3	6.75	1.06	43.8×10^3	3.0×10^3	21.25	—	2.48	54.3×10^3	0.8×10^3	26.35	—	3.08
3450	20.9	0.1	6.06	1.12	63.5	5.7	18.4	—	3.84	72.7	8.9	21.05	—	5.17
5660	29.1	1.1	5.14	1.21	88.8	12.6	15.7	—	6.45	109.6	12.9	19.35	—	9.16
7160	33.2	0	4.64	1.29	105.7	17.2	14.75	2,3	8.50	136	25.7	19.0	2.3	12.3
9880	40.3	0.9	4.08	1.45	142.6	33	14.45	2,7	13.10	190.2	42.7	19.25	2.3	19.45
11090	42.6	1.1	3.84	1.50	—	—	—	—	—	215	52	19.4	2.4	23.0
0	$w_{289°} = 0.00209\ \Omega$				$w_{90°} = 0.00097\ \Omega$					$w_{74°.5} = 0.00088\ \Omega$.				

TABLE V.

HALL effect, asymmetry and resistance change for $Bi_{p\,II}$.

H	$T = 289°$ K.				$T = 90°$ K.					$T = 73.0°$ K.				
	RH	D	$-R$	$\left[\frac{w'}{w}\right]_T$	RH	D	$-R$	Q	$\left[\frac{w'}{w}\right]_T$	RH	D	$-R$	Q	$\left[\frac{w'}{w}\right]_T$
2060	18.7×10^3	0.1×10^3	9.08	1.023	74.3×10^3	0.9×10^3	36.1	—	1.295	94.4×10^3	1.3×10^3	45.85	—	1.386
3450	28.2	0.1	8.17	1.057	110.7	1.5	32.1	—	1.59	139.5	3.5	40.4	—	1.727
5660	39.8	0.2	7.05	1.108	155.2	6	27.4	—	—	205	8.5	36.2	—	2.355
7160	46.1	0.2	6.44	1.148	185.8	10	25.95	0.68	2.47	248	14	34.6	0.76	2.787
8520	52.1	0.4	6.12	1.186	214.2	14	25.15	0.74	2.89	289	17	33.9	0.73	3.255
9880	55.9	0.1	5.66	1.222	243.0	18	24.6	0.79	3.28	330.5	20	33.5	0.75	3.718
11090	59.9	0.4	5.41	1.260	267.3	22	24.1	0.82	3.67	367	24	33.1	0.78	4.12
12090	62.8	0.7	5.19	1.287	288.0	24	23.8	0.82	3.94	398	29	32.9	0.82	4.485
0	$w_{289°} = 0.00389\ \Omega$				$w_{90°} = 0.00444\ \Omega$					$w_{73°} = 0.00455\ \Omega$				

Figs. 3 and 4 show the resistance increase, and fig. 5 the Hall effect as function of the field for various temperatures. [1]

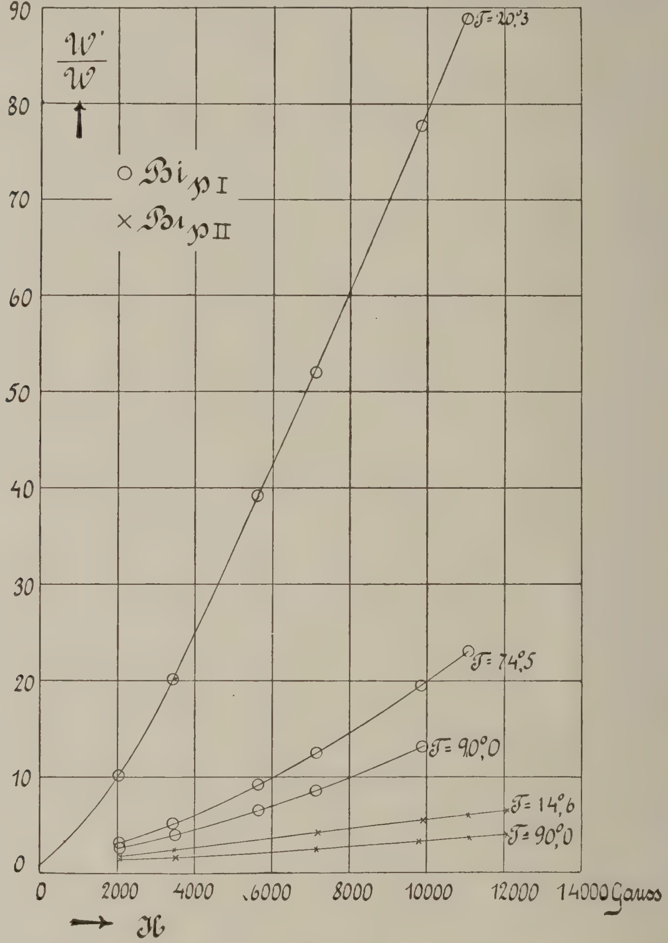

Fig. 3.

The isotherms of the magnetic increase of resistance are of the same nature as those for Bi_{dI}, but the rectilinear portion of the curve now begins at 7 kilogauss. Equation (2) also holds in this case for the region $90°\ K \geqq T > 15°K$. This is evident from Table VI.

---

[1] Remembering that $RH = \frac{Ed}{I}$ where E is the Hall potential difference, d the thickness of the plate, and I the main current, we see that RH is the Hall potential difference for $d = 1$ and $I = 1$.

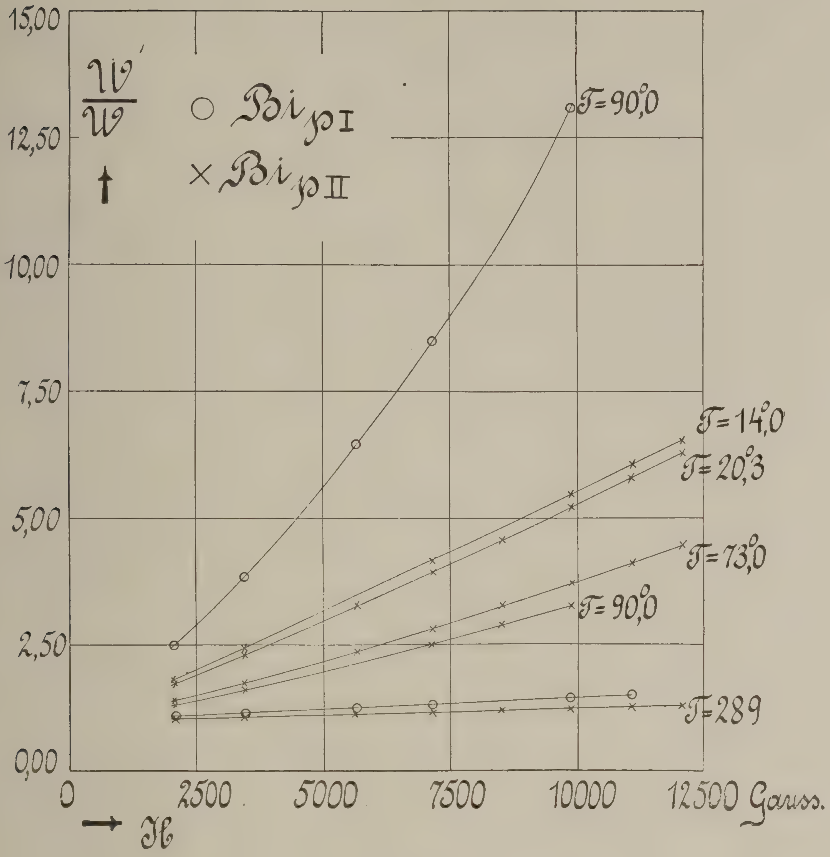

Fig. 4

TABLE VI.

a for *Bi*.

Bi_{pI}			Bi_{pII}		
T	$a_{Obs.}$	$a_{Calc.}$	T	$a_{Obs.}$	a_{Calc}
90° K	1.69	1.77	90° K	29.3	31
74°.5	2.7	2.55	73°	35.8	34.4
20°.3	9.2	9.1	20°.3	47.3	47.3
			14°.6	48.3	49

The diminution of the resistance at low temperatures without a magnetic field is practically the same for both Bi_{pI} and Bi_{dI}.

In liquid air the magnetic increase of resistance, however, appears to be much greater for Bi_{dI}, just as was found to be the case in liquid hydrogen [1]).

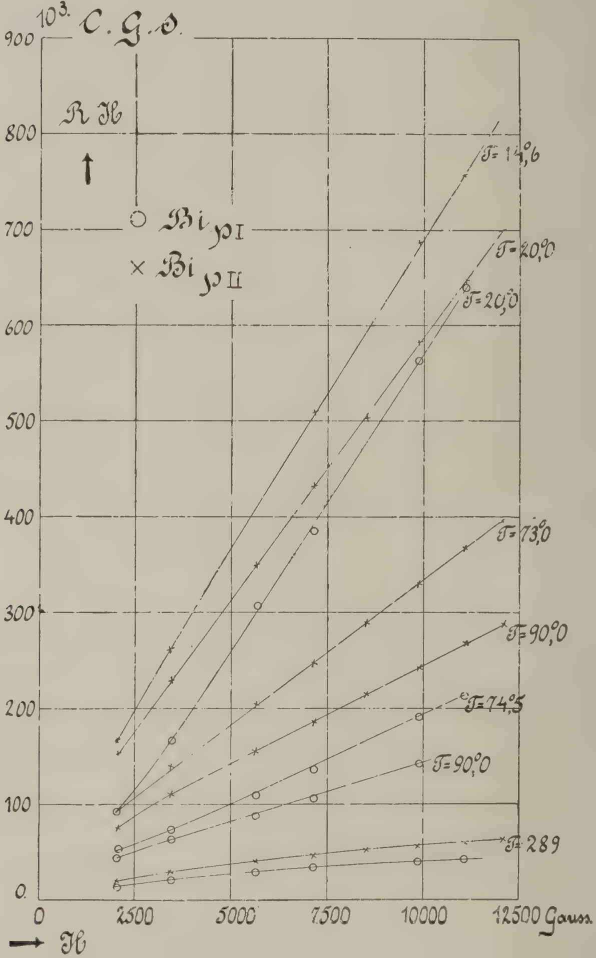

Fig. 5.

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[1]) H. Kamerlingh Onnes and Bengt Beckman, Comm. No. 129*a*.

For $H = 11090$ we find at

	Bi_{dI}	Bi_{pI}	Bi_{pII}
$T = 90°$ K.	$\frac{w'}{w_0} = 11.6$	7.5	3.25
$T = 20°.3$ K.	$\frac{w'}{w_0} = 42$	19.7	4.7

For Bi_{pII} the resistance temperature coefficient with no magnetic field is negative, which undoubtedly points to the presence of impurity.

At $T = 289°$K. the specific resistance of Bi_{pI} is about 1.5×10^5, and for Bi_{pII} 2.3×10^5 *C.G.S.*

The magnetic change of resistance is much smaller for Bi_{pII}, particularly so at low temperatures.

Just as in the experiments in liquid hydrogen, for $H > 3000$ RH becomes a linear function of the field

$$RH = a'H + b' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Following J. Becquerel [1]) we may regard the Hall effect for bismuth as resulting from two components. One of these is proportional to the field, and was always negative for the plates (Bi_{pI}, Bi_{pII}) I used. The other is constant or, as one may say, saturated, for these plates from $H = 3000$ upwards.

Within the temperature region

$$90°\text{K} \geq T > 15°\text{ K}$$

a' can, to a first approximation, be satisfactorily represented by

$$a' = a_0' \, e^{-\beta T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The agreement for $T = 90°$K. between observation and calculation from (3) with $a' = 20.6$ and $b' = 39.3 \times 10^3$ for the plate Bi_{pII} is exhibited in Table VII, while Table VIII shows how far the relationship (4) holds.

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[1]) J. Becquerel: C. R. **154**, 1795, 1912.

TABLE VII.

Linear variation of the HALL effect in strong fields for Bi_{pII} at $T = 90°$ K.

H	$RH_{Obs.}$	$RH_{Calc.}$
3450	110.7×10^3	110.4×10^3
5660	155.2	155.8
7160	185.8	186.8
8520	214.2	214.8
9880	243.0	242.8
11090	267.3	267 8
12090	288.0	288.3

TABLE VIII.

a' for Bi_{pI}			a' for Bi_{pII}		
T	$a'_{Obs.}$	$a'_{Calc.}$	T	$a'_{Obs.}$	$a'_{Calc.}$
90° K.	12.4	12.1	90° K.	20.6	22.0
74°.5	17.7	17.4	73°	29.8	27.6
20°.3	62.1	62.6	20°.3	54.3	57 3
			14°.6	64 5	62.4

The constant b' which gives the value of the second component of the effect in the state of saturation is commonly negative. Only for Bi_{pI} at hydrogen temperatures does it become positive. With Bi_{pII} b' is almost constant for $T \leqq 90°$ K.; with Bi_{pI} b' is very small and for $T \geqq 72°$ K. is practically constant.

In strong fields the constant R approaches a limiting value in accordance with equation (3). In weak fields RH for Bi_{pI} is inversely proportional to the temperature at $T = 289°$ K., $90°$ K., 74.°5 K.

Tables IV and V also contain the quantity $Q = \dfrac{D}{\dfrac{w'}{w} - 1}$. For $H > 7000$, Q is either a linear function of the field, or a constant [1].

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[1] Cf. E. v. EVERDINGEN; Comm. Suppl. N⁰. 2 p. 57.

COMMUNICATIONS

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 130b.

BENGT BECKMAN. — On the HALL effect, and on the change in resistance in a magnetic field at low temperatures. IV. Measurements at temperatures between + 17° C. and — 200° C. of the HALL effect, and of the change in the resistance of metals and alloys in a magnetic field. (*Continued*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **26 October 1912,** p. 672—676).

EDUARD IJDO — PRINTER — LEIDEN.

BENGT BECKMAN. — *On the* HALL *effect, and on the change in resistance in a magnetic field at low temperatures.* IV. *Measurements at temperatures between + 17° C. and — 200° C. of the* HALL *effect, and of the change in the resistance of metals and alloys in a magnetic field. (Continued).*

(This Communication is a continuation of Comm. N^0. 130a in which the behaviour of bismuth was discussed.)

II. *Gold, Silver, Copper, Palladium.*

§ 4. HALL *effect for Gold.* From the temperature decrease of the resistance without magnetic field[1]), $\frac{w_{T=20}}{w_{T=273}}=0.035$, it is to be supposed that this plate is composed of purer gold than that of the wire Au_0 of Comm. N^0. 99, which was known to contain 0.03$^0/_0$ impurity. The thickness of the plate was 0.101 mm.

TABLE IX.
HALL effect for Gold Au_{pl}.

$T = 290°$ K.			$T = 90°$ K.			$T = 77°$ K.		
H	RH	$-R \times 10^4$	H	RH	$-R \times 10^4$	H	RH	$-R \times 10^4$
7730	5.62	7.27	7730	5.82	7.53	4940	3.75	7.59
9500	6.75	7.11	9500	7.24	7 62	9065	6.95	7.67
11080	8.11	7.32	11080	8.53	7.70	10270	7.72	7 59
12200	8.85	7.25	12200	9.24	7.58			
$w_{290°} = 202 \times 10^{-6}\ \Omega$			$w_{90°} = 54.6 \times 10^{-6}\ \Omega$					

§ 5 HALL *effect for Silver.* The plate Ag_{pl} was found to be of practically the same purity as that of the wire Ag_{I} of Comm.

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[1]) H. KAMERLINGH ONNES and BENGT BECKMAN; Comm N^0. 129a.

N°. 99 which contained 0.18 °/₀ impurity. The thickness of the plate was 0.096 mm.

TABLE X.
HALL effect for Silver Ag_{pI}.

H	$T = 299°$ K.		$T = 90°$ K.	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$
4940	3.97	8.04	4.10	8.30
7260	5.81	8.01	5.92	8.15
9065	7.23	7.98	7.45	8.22
10270	8.16	7.95	8.38	8.16
$w_{290°} = 173 \times 10^{-6}\,\Omega$			$w_{90°} = 37 \times 10^{-6}\,\Omega$	

§ 6. HALL *effect for electrolytic Copper.* The thickness of the plate Cu_{pI} was 0.057 mm.

TABLE XI.
HALL effect for Copper Cu_{pI}.

H	$T = 290°$ K.		$T = 90°$ K.	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$
7260	3.59	4.95	4.05	5.58
9065	4.42	4.87	5.04	5.56
10270	5.08	4.95	5.66	5.51
0	$w_{290°} = 312 \times 10^{-6}\,\Omega$		$w_{90°} = 54 \times 10^{-6}\,\Omega$	

§ 7. HALL *effect for Palladium.* The thickness of the plate was 0.100 mm

TABLE XII.

HALL effect for Palladium Pd_{pI}.

H	$T = 290°$ K.		$T = 90°$ K.	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$
8250	5.61	6.80	5.85	7.10
9065	6.04	6.66	6.35	7.01
9760	6.64	6.80	6.77	6.94
10090	—	—	7.06	7.00
0	$w_{290°} = 126 \times 10^{-5}\ \Omega$		$w_{90°} = 70 \times 10^{-5}\ \Omega$	

§ 8. *Summary of the variation of the* HALL *coefficient for different metals.* The results obtained in §§ 4—7 are collected in Tables XIII and XIV. For R is taken at each temperature the mean of the values [1]) for the different fields.

TABLE XIII.

HALL coefficient R.

T	Au_{pI}	Ag_{pI}	Cu_{pI}	Pd_{pI}
290° K.	7.2×10^{-4}	8.0×10^{-4}	4.9×10^{-4}	6.75×10^{-4}
90°	7.6	8.2	5.6	7.0
77°	7.6	—	—	—

---

[1]) It has not been possible to determine the thickness of the plates with an accuracy greater than about 3 %, which of course influences the absolute values of the HALL coefficients. This inexactitude, however, makes no difference in the temperature coefficient of the HALL effect, the measurement of which has been the principal object of this investigation.

TABLE XIV.

Variation of the Hall coefficient $\frac{R_T}{R_{290^\circ}}$

T	Au_{pI}	Ag_{pI}	Cu_{pI}	Pd_{pI}
290° K.	1	1	1	1
90°	1.05	1.025	1.13	1.035
77°	1.05	—	—	—

From these observations, therefore, the Hall coefficient for *Au*, *Ag* and *Pd* is almost constant from ordinary temperature down to that of liquid air. A distinct increase is first observed on proceeding to hydrogen temperatures [1]), which amounts to 25 — 35 % for Gold, Silver and Copper, and 100 % in the case of Palladium.

A. W. Smith [2]) gives the following values for the ratio $\frac{R_{83^\circ K}}{R_{293^\circ K}}$

for	*Au*	*Ag*	*Cu*	*Pd*
	1.03	1.095	1.205	1.27

This gives agreement in the case of *Au* but with *Ag* and *Cu*, and particularly with *Pd*, Smith's results deviate considerably from mine. In the case of *Cu* and *Ag* the lack of agreement may perhaps be ascribed to the presence of impurity.

The relationship $R_0 = \frac{3\pi}{8N\varepsilon}$ deduced for the Hall effect by R. Gans [3]) has been utilised by J. Koenigsberger and J. Weiss [4]) to obtain the variation of the electron density *(N)* from the temperature coefficient of the Hall effect. From this relation it should follow that the density of the electrons in *Au*, *Ag*, *Cu*, *Pd* varies very slowly with the temperature, much more slowly than $\sqrt{T}$.

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[1]) H. Kamerlingh Onnes and Bengt Beckman: Comm. N°. 129*a*.

[2]) A. W. Smith: Phys. Rev. **30**, 1, 1910.

[3]) R. Gans: Ann. d. Phys: **20**, 293, 1906.

[4]) J. Koenigsberger and J. Weiss: Ann. d. Phys: **35**, 1, 1911.

III. *Alloys.*

§ 9. *Gold-Silver.* The alloy investigated contained 2°/$_0$ of silver by volume.

TABLE XV.

Hall effect for a gold-silver alloy.

H	$T = 290°$ K.		$T = 90°$ K.	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$
8250	5.59	6.77	5.40	6.55
9065	6.18	6.82	6.02	6.64
9760	6.60	6.77	6.44	6.60
10270	6.94	6.76	6.86	6.67
0	$w_{290°} = 3.81 \times 10^{-4}\,\Omega$		$w_{90°} = 1.77 \times 10^{-4}\,\Omega$	

Hence the mean value of R

for $T = 290°$ K. is $R = 6.78 \times 10^{-4}$

90° $R = 6.61$

The hydrogen experiments gave [1])

for $T = 20°.3$ K. $R = 6.71 \times 10^{-4}$

14°.5 $R = 6.48$

Hence the **Hall** coefficient for this alloy is almost constant; on proceeding to low temperatures it begins to exhibit a slight *decrease.*

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[1]) H. Kamerlingh Onnes and Bengt Beckman: Comm. N°. 129*a*.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory

No. 130c.

H. KAMERLINGH ONNES and **BENGT BECKMAN**. — On the HALL effect and the change in resistance in a magnetic field at low temperatures. V. Measurements on the HALL effect for alloys at the boiling point of hydrogen and at lower temperatures.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **26 October 1912**, p. 676—678).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and **BENGT BECKMAN**. — *On the* HALL *effect and the change in resistance in a magnetic field at low temperatures.* V. *Measurements on the* HALL *effect for alloys at the boiling point of hydrogen and at lower temperatures.*

VI. *Gold-silver alloys.*

§ 16 [1]. In § 12 of Comm. No. 129*a* observations on the HALL effect for an alloy of gold and silver $(Au—Ag)_{\mathrm{I}}$ with 2 % of *Ag* by volume are published. We now give the results of our measurements on two *Au—Ag* alloys, containing greater percentages of silver.

The alloy $(Au—Ag)_{\mathrm{II}}$ was made by fusing 9 % by volume of silver with gold [2]. The thickness of the plate was 0.049 mm. The HALL effect was measured at the temperatures $T = 290°$, 20°.3 and 14°.5 K.

We found:

TABLE XV.

The HALL effect for $(Au—Ag)_{\mathrm{II}}$

H	$T = 290°$ K.		$T = 20°.3$ K.		$T = 14°.5$ K.	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$	RH	$-R \times 10^4$
8250	4.60	5.58	3.07	3.72	3.05	3.69
9360	5.47	5.61	3.47	3.71	3.52	3.76
10270	5.71	5.56	3.82	3.72	3 83	3.73
0	$w = 8.06 \times 10^{-4}\,\Omega$ $\frac{w}{w_0} = 1.019$		$w = 4.58 \times 10^{-4}\,\Omega$ $\frac{w}{w_0} = 0.579$		$w = 4.54 \times 10^{-4}\,\Omega$ $\frac{w}{w_0} = 0.574$	

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[1] The sections of this paper are numbered in continuation of those of Comm. N°. 129*c*.

[2] The exact analysis is to be published later.

The alloy $(Au - Ag)_{III}$ was formed by fusing 30 % by volume of silver with gold[1]. The thickness of the plate was 0.078 mm. We found:

TABLE XVI.

The HALL effect for $(Au—Ag)_{III}$

H	$T = 290°$ K.		$T = 20°.3$ K.		$T = 14°.5$ K.	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$	RH	$-R \times 10^4$
8250	4.61	5.60	3.00	3.63	3.12	3.78
9360	5.23	5.59	3.30	3.53	3.42	3.66
10270	5.67	5.52	3.72	3.62	3.81	3.71
0	$w = 9.47 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 1.013$		$w = 7.05 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 0.754$		$w = 7.02 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 0.751$	

The results of measurements on gold and on the three gold-silver alloys are brought together in the Tables XVII and XVIII.

TABLE XVII.

The HALL coefficient for gold and gold-silver alloys.

T	Au_{pI}	$(Au—Ag)_I$	$(Au—Ag)_{II}$	$(Au—Ag)_{III}$
290° K.	7.2×10^{-4}	6.8×10^{-4}	5.6×10^{-4}	5.6×10^{-4}
20°.3	9.8	6.7	3.7	3.6
14°.5	9.8	6.5	3.7	3.7

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[1] The exact analysis is to be published later.

TABLE XVIII.

Change of the HALL coefficient $\frac{R_T}{R_{290^\circ}}$ on cooling to and in the region of liquid hydrogen temperatures.

T	Au_{pI}	$(Au-Ag)_I$	$(Au-Ag)_{II}$	$(Au-Ag)_{III}$
290° K	1	1	1	1
20°.3	1.355	0.985	0.665	0.646
14°.5	1 355	0.955	0.665	0.667

Thus, $\frac{R_{T=20.3}}{R_{T=290}}$ diminishes by greater percentages of silver. For pure gold $R_{T=20.3} > R_{T=290}$, but for alloys with more than 2 % of silver by volume $R_{T=20.3} < R_{T=290}$.

The curve that represents the relation between the HALL coefficient $R_{T=20.3}$ and the percentages of silver is of a shape analogous to that representing the conductibilily or the temperature coefficient of the resistance as a function of percentages of silver. The curve for $R_{T=20.3}$ at first descends very rapidly for small admixtures of *Ag*; at higher concentrations it becomes flatter.

The HALL coefficient $R_{T=20.3}$ is approximately a linear function of the quantity $\frac{w_{T=20.3}}{w_{T=273}}$ for alloys with less than about 8% by volume of *Ag*.

The HALL coefficient $R_{T=290}$ diminishes too though much more slowly than $R_{T=20.3}$, when the percentage of *Ag* increases.

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UNIVERSITY OF [illegible]
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COMMUNICATIONS
FROM THE
PHYSICAL LABORATORY
OF THE
UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 131a.

E. MATHIAS, H. KAMERLINGH ONNES and **C. A. CROMMELIN**. On the rectilinear diameter for argon.

(*Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling der Kon. Akademie van Wetenschappen te Amsterdam*, **26 October 1912**, p. 700—706, **30 November 1912**, p. 893—898).

EDUARD IJDO — PRINTER — LEIDEN.

E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN.

On the rectilinear diameter for argon.

§ 1. *Introduction.* The present paper forms a continuation of the investigation of the diameter for substances of low critical temperature with which a beginning was made with oxygen [1]). The importance of this and of similar investigations was indicated in the introduction to the communication referred to, so that we need not discuss the point further here.

We chose argon for the present investigation since the isotherms for that gas had already been determined to within the neighbourhood of the critical point, while the critical point itself, the vapour pressures and even preliminary values of the densities of the coexisting vapour and liquid phases were already known [2]); the monatomic nature of the gas, moreover, will undoubtedly enhance the value of the results.

§ 2. *Apparatus.* The apparatus was essentially the same as that employed in the investigation of oxygen. The arrangement for compressing the argon and also the volumenometer have, however, undergone some modification since that time, so that it seemed desirable to take this opportunity of publishing a new diagram of the whole apparatus (Fig. 1).

The modifications of the volumenometer and of the auxiliary apparatus belonging to it have already been described in full detail [3]).

The use of such a costly gas as pure argon necessitated, however, a completely new arrangement of the pressure connections. The

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[1]) E. Mathias and H. Kamerlingh Onnes, Comm. No. 117. C. R. 151, p. 213 and 477, 1910.

[2]) C. A. Crommelin, Comm. No. 115, H. Kamerlingh Onnes and C. A. Crommelin, Comm. N°. 118 and C. A. Crommelin, Thesis for the doctorate, Leiden 1910.

[3]) W. J. de Haas, Comm. No. 121*a*, H. Kamerlingh Onnes and W. J. de Haas, Comm. N°. 127*c* and W. J. de Haas, Thesis for the Doctorate, Leiden 1912, in which diagrams of the modified volumenometer are also given. Certain small errors in these diagrams make it desirable to publish a diagram here in which these errors are corrected.

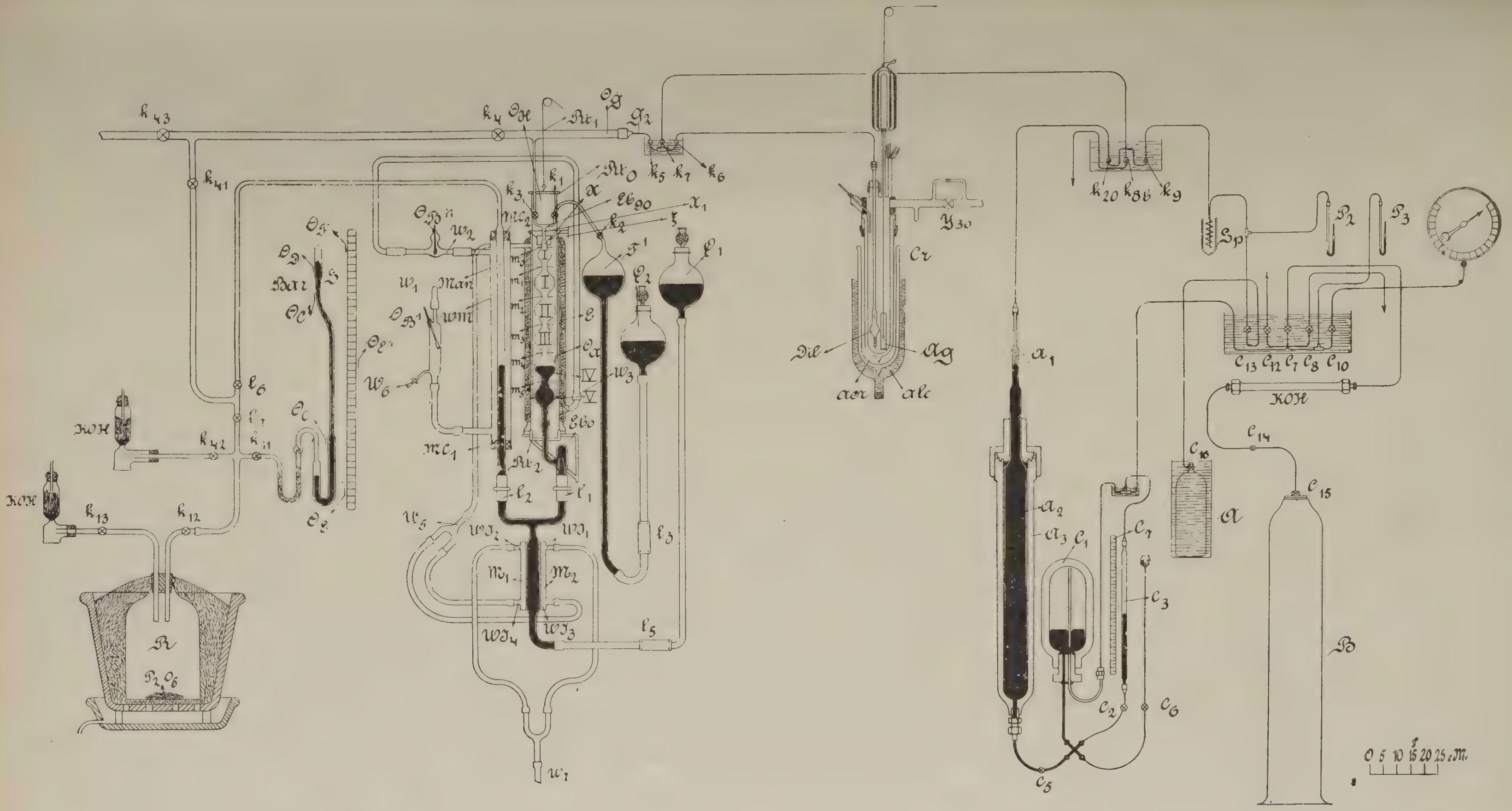
k43
k4
k41
k6
k7
k42
k11
k13
k12
KOH
KOH
R
P2O5
Man
wm
W1
W2
W3
W6
W7
k1
k2
k3
k5
k6
k7
l1
l2
l3
l5
F1
Q1
Q2
I
II
III
IV
V
E
Eb0
Eb90
x1
Cr
y30
Dil
Ag
k20
k8b
k9
Sp
P2
P3
c13
c12
c7
c8
c10
KOH
c14
c15
c16
A
B
a1
a2
a3
c1
c2
c3
c5
c6
cr
0 5 10 15 20 25 cM

Fig. 1

copper tubes of which all the connections were made were chosen as narrow as possible so as to reduce the quantity of gas in the dead space to a minimum. The argon was contained in the steel cylinder A which was completely immersed in oil; so too were all the taps and coupling pieces which contained compressed gas [1]).

Through the taps C_{16} and C_{13}, the gas passes to the spiral Sp; here the argon is dried by immersing this spiral in alcohol and cooling it down to its melting point by means of liquid air. Through k_9 and k_{10} the gas then reaches the compression tube A_2 within the compression cylinder A_3 [2]). In this compression tube the mercury is forced by means of compressed air from the steel cylinder B; by this the required amount of argon is compressed into the dilatometer on closing the tap k_9 and opening k_7 and k_6. This arrangement for compressing pure gases has already been fully described in previous communications [3]); moreover, its mode of operation is easily seen from the accompanying diagram.

Through the tap C_{12} it was possible to establish communication between the air compressor and our accurate closed hydrogen manometer [4]), and by this means we were able during the actual measurements to obtain a few further determinations of the vapour pressure, which will be published shortly.

The cryostat Cr was the same as that used in the investigation of oxygen, the sole modification being the introduction of a different type of stirrer, Ag, provided with valves [5]).

As the appendix of the dilatometer formerly used was found to be too narrow, another dilatometer Dil, very accurately calibrated, was employed with an appendix sufficiently wide to allow of the suitable measurement of the small volume of the liquid coexisting with the vapour.

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[1]) H. Kamerlingh Onnes, Comm. No. 94*b*. The value of this device for the detection of leaks has already been repeatedly emphasized.

[2]) At the cylinder A is connected the glass manometer P_2 for high pressures and of small volume, especially constructed for the use of such cylinders as reservoirs for the rare gases.

[3]) H. Kamerlingh Onnes and H. H. F. Hyndman, Comm. No. 69, and H. Kamerlingh Onnes and C. Braak, Comm. No. 97*a*.

[4]) H. Kamerlingh Onnes and H. H. F. Hyndman, Comm. No. 78, and H. Kamerlingh Onnes and C. Braak, Comm. No. 97*a*.

[5]) H. Kamerlingh Onnes, Comm. No. 123.

A GAEDE vacuum pump was used, and we found it of the greatest utility, particularly during the actual measurements, in ensuring the continued absence of leaks.

Two platinum resistance thermometers were introduced into the cryostat to serve for the regulation and measurement of the temperature.

The argon used for the present measurements was taken from the same supply as that employed in the previous investigations already quoted. The impurity in this argon is certainly less than 0.1 $^0/_0$ [1]).

§ 3. *Experiments* We may now give a short description of the sequence of operations involved in the measurements:

1. All the apparatus and connections were reduced to a high vacuum and then washed out with argon.

2. The cryostat was filled with the liquid gas desired (O_2, CH_4, or $C_2 H_4$).

3. The argon was admitted to the compression tube A_2 and then pumped into the dilatometer.

4. The argon meniscus was adjusted to the upper part of the stem of the dilatometer, and the tap k_6 was closed.

5. When the temperature is constant the position of the argon meniscus is read, the temperature is measured, and also when required, the pressure registered by the hydrogen manometer.

6. By reducing the pressure in the cryostat transition is made to a lower temperature, the same measurements are repeated; a lower temperature is then installed and so on until the meniscus has sunk below the subdivided portion of the stem.

7. Sufficient argon is then allowed to escape into the volumenometer to bring the meniscus to the lower part of the appendix below the dilatometer; the temperature, pressure and volume of the escaped gas are measured.

8. The measurements of 5. and 6. are repeated in the reversed order of temperature until the meniscus reaches the upper part of the appendix.

9. The argon still remaining in the dilatometer is transferred to

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[1]) For a detailed description of the preparation and of the analysis of this argon see C. A. CROMMELIN, Thesis for the Doctorate, Leiden, 1910.

the volumenometer, and the measurements of 7. are repeated.

It is clear that these measurements yielded the data requisite for the calculation of the liquid and vapour densities at all the experimental temperatures. To these calculations we shall return in the succeeding section.

The dimensions of the dilatometer were so calculated that one could finish off the temperature range for any particular substance in the cryostat by successive measurements; in this way only two measurements with the volumenometer were required to give both the liquid and vapour densities.

§ 4 *Calculations.* In many respects the calculations were made in the same way as those of Comm. No. 117. It was of great advantage to us that so many data are already available for argon, and that we could already make use of the reduced equation of state, VII. A. 3. [1]). We shall here give a short summary of the method adopted in the calculations.

Working from the very accurate calibration of the dilatometer, the *liquid volumes* were first calculated directly from the positions of the meniscus top in the stem and in the appendix, without applying any correction. To the numbers so obtained the following corrections were then applied:

1. A fairly large correction for the diminution of the volume of the dilatometer at low temperature, seeing that the calibration of the dilatometer had been reduced to + 20° C.; the correction was obtained by means of a formula from a former communication [2]).

2. A correction for the increase of volume of the dilatometer due to the pressure. For this correction, which was so small as to be negligible in almost every case, approximate values were calculated from data contained in two previous communications [3]).

3. A correction for the volume of the argon meniscus. KELVIN'S graphical method [4]) was employed for the evaluation of this by no

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[1]) H. KAMERLINGH ONNES and C. A. CROMMELIN, Comm. No. 128.

[2]) H. KAMERLINGH ONNES and J. CLAY, Comm. No. 95*b*.

[3]) Comm. No. 78 and 97*a*.

[4]) The capillary constant for argon and its variation with temperature must be known for the construction of the diagrams. Now BALY and DONNAN (Journ. of the Chem. Soc. Trans. 81, 907. 1902) have determined capillary constants for

means negligible correction. To obtain the volume of the menisci it was usually sufficient for our purpose to regard the surface of the liquid as half of an oblate ellipsoid of revolution. Only at the higher temperatures was it necessary to apply Guldin's theorem to the Kelvin diagram in order to determine the body of revolution.

Having thus calculated all the liquid volumes, we were able, taking the first two of the above corrections into account, to obtain *the volumes of the saturated vapour*. In this it was assumed that the temperature of the bath extended to a distance of 2 cms. above the surface of the liquid.

The following method was adopted of *reducing the gaseous argon* in the glass and steel capillaries from the point of the capillary just mentioned up to the tap k_6 *to terms of the normal volume*. The portion of the glass capillary within the cryostat was divided into different parts for each of which the mean temperature was known from previous papers [1]). The temperatures of the part of the glass capillary outside the cryostat and of the steel capillary up to the tap k_6 were obtained from thermometers during the measurements. The volumes of all these portions were known from the calibrations

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liquid argon but only between — 189° C. and — 183° C. so that the question now arose as to how to interpolate in the most rational manner possible from — 183° C. to the critical temperature. A comparison between the results giving the reduced capillary constant $\frac{\psi_\sigma}{T_k^{1/3} p_k^{2/3}}$ (see J. D. van der Waals, Cont. I. p. 176) as a function of the reduced temperature by Baly and Donnan (l.c.), for argon, by de Vries (Comm. No 6, and Thesis for the doctorate, Leiden 1893) for ether, by Verschaffelt (Comm. No. 18) for carbon dioxide and nitrous oxide was fruitless, seeing that the last three correspond well, while argon deviates strongly from them. A suitable rational method is given by the assumption of the validity of the Eötvös formula (Ann. d. Phys. und Chem. 27 (1886) p. 448) according to which the quantity $\psi_\sigma \left(\frac{M}{\rho_{liq}}\right)^{\frac{2}{3}}$ is a linear function of the temperature. According to Baly and Donnan we get for argon $\psi_\sigma \left(\frac{M}{\rho_{liq}}\right)^{\frac{2}{3}} = 2.020\ (145.44 - T)$; from this formula our estimates have been made except that for the highest temperature, ± — 125° C., at which one is so close to the critical temperature that the Eötvös formula no longer holds, and for which interpolation was resorted to in correspondence with the curves given by other substances.

[1]) C. Braak, Thesis for the doctorate, Leiden. 1908, p. 16.

and the pressures from the vapour pressures already published [1]) together with those added by the present measurements.

In order now to obtain the normal volume of all these portions at different temperatures we again make use of the modified series

$$pv_{\mathrm{N}} = A_{\mathrm{N}} \{1 + B^{(p)} p + C^{(p)} p^2 + \ldots\}$$

Since $v_{\mathrm{N}} = \frac{V}{\mathrm{N}}$ and $A_{\mathrm{N}} = A_{\mathrm{N}\,0^{\circ}\mathrm{C.}}\,(1 + \alpha_{\mathrm{A}} t)$, it follows that

$$\mathrm{N} = \frac{p V}{A_{\mathrm{N}\,0^{\circ}\mathrm{C}}\,(1 + \alpha_{\mathrm{A}}\, t)\,[1 + B^{(p)} p + C^{(p)} p^2]}\ {}^{2)}$$

The virial coefficients necessary for the employment of this equation were taken from the equation VII. A. 3. In all these calculations the coefficient $C^{(p)}$ could be neglected.

We may again refer to previous papers [3]) for the corrections which have to be applied to the volumenometric determinations.

For the normal specific mass of argon we used the value given by RAMSAY and TRAVERS [4]) 0.001782.

We may further state that at the lowest three temperatures the vapour densities were not measured but calculated; in view of the degree of accuracy desired this is quite permissible. The calculation was made by means of the above series in which, however, $C^{(p)}$ is now no longer negligible.

§ 5. *Results.* The results obtained are given in the table on the next page [5]).

The calculated values of the ordinates of the diameter given in this table have been obtained from the equation

$$D_{\rho\Gamma} = 0.20956 - 0.0026235\, t.$$

The diameter has been drawn through the points — 175°.39 and — 131°.54.

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[1]) C. A. CROMMELIN, Comm. No. 115.

[2]) In these formulae p is the pressure in atmospheres, v_{N} the volume expressed in terms of the normal volume as unit, N the normal volume, V the actual experimental volume and α_{A} the coefficient of expansion in the AVOGADRO state, 0.0036618. For the notation see also H. KAMERLINGH ONNES and W. H. KEESOM, Suppl. No. 23.

[3]) Comm. No 121*a*, and 127*c* and W. J. DE HAAS, Thesis for the doctorate, 1912.

[4]) W. RAMSAY and M. W. TRAVERS, Proc. R. S. 67, 329, 1900.

[5]) For the notations, see Suppl. No. 23.

bath	$\theta = T - T_{0^\circ C.}$ Kelvin degrees	$\rho_{liq\Gamma}$	$\rho_{vap\Gamma}$	$D_{\rho\Gamma}(O)$	$D_{\rho\Gamma}(C)$	O—C
O_2	— 183.15	1.37396	0.00801	0.69099	0.69006	+ 0.00093
CH_4	— 175.39	1.32482	0.01457	0.66970	0.66970	
CH_4	— 161.23	1.22414	0.03723	0.63069	0.63255	— 0.00186
C_2H_4	— 150.76	1.13851	0.06785	0.60318	0.60508	— 0.00190
C_2H_4	— 140.20	1.03456	0.12552	0.58004	0.57738	+ 0.00266
C_2H_4	— 135.51	0.97385	0.15994	0.56690	0.56507	+ 0.00183
C_2H_4	— 131.54	0.91499	0.19432	0.55466	0.55466	
C_2H_4	— 125.17	0.77289	0.29534	0.53412	0.53794	— 0.00382

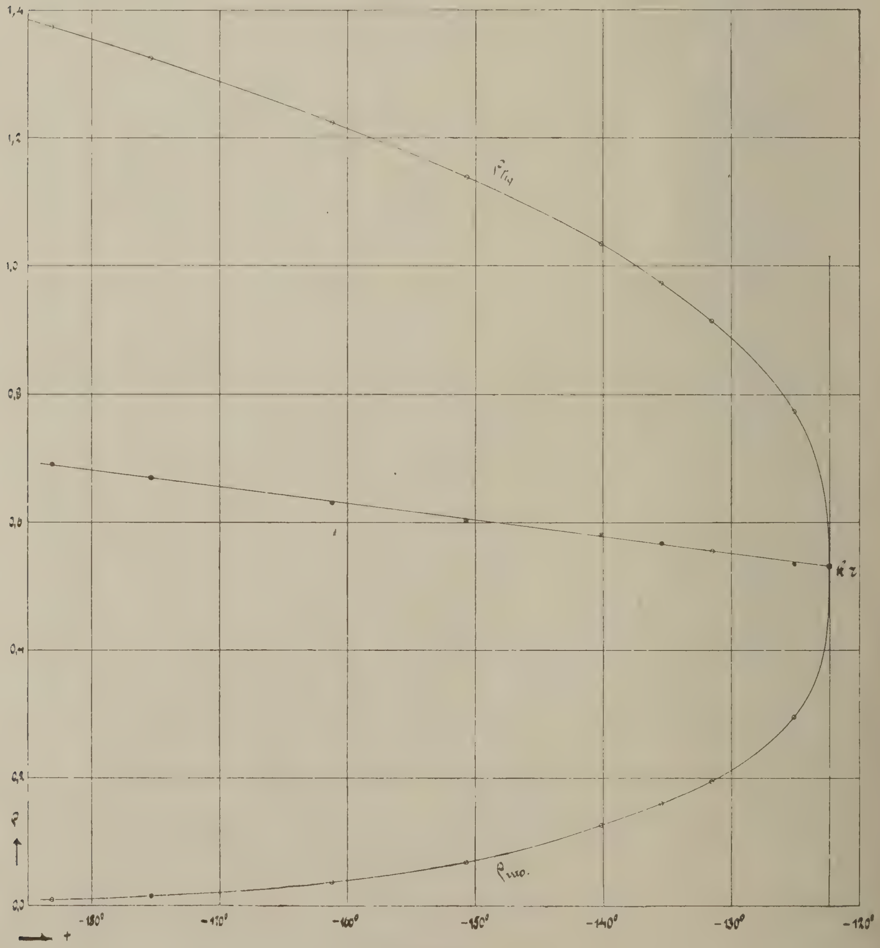

Fig. 2.

§ 6. *Discussion.* The slope of the diameter is given by

$$b_{dr} = -0.0026235.$$

This coefficient is very large, larger than has been found for any other substance yet investigated with the exception of xenon, for which PATTERSON, CRIPPS and WHYTLAW-GRAY [1]) have found — 0.003055. Comparison of the values of this constant for the two monatomic substances argon and xenon again reveals the influence exerted upon it by the value of the critical temperature.

With respect to the critical density the following remarks must be made: if we assume that the diameter remains rectilinear right up to the critical point, we then find

$$\rho_{kd} = 0.53078.$$

Using the equation

$$\left(\frac{\partial p}{\partial T}\right)_{vk} = \left(\frac{dp}{dT}\right)_{\text{koex. k.}}$$

the value

$$\rho_{ks} = 0.509$$

was previously found from the argon isotherms [2]). The difference between these two values is of the same order of magnitude and is in the same direction as the differences found for other substances, carbon dioxide [3]), methyl chloride [4]), amongst others. The fairly large deviation from rectilinearity of the experimental diameter apparent in the neighbourhood of — 125°.17 agrees well with this behaviour. A similar curvature in the diameter in the immediate neighbourhood of the critical point showed itself for carbon dioxide in the measurements of KEESOM [5]) and was confirmed [6]) by comparison with those of KAMERLINGH ONNES and FABIUS [7]), and was recently investigated more closely by CARDOSO [8]) for sulphur dioxide.

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[1]) PATTERSON, CRIPPS en WHYTLAW-GRAY, Proc. R. S. (A.) 86. (1912) pg. 579.

[2]) C. A. CROMMELIN, Comm. No. 118*a* and Thesis for the doctorate, Leiden, 1910.

[3]) W. H. KEESOM, Comm. No. 88; H. KAMERLINGH ONNES and W. H. KEESOM, Comm. No. 104*a*.

[4]) C. H. BRINKMAN, Thesis for the doctorate, Amsterdam, 1904.

[5]) W. H. KEESOM, Comm. No. 88. See Plate I Comm. No. 104*a*.

[6]) H. KAMERLINGH ONNES and W. H. KEESOM, Comm. No. 104*a*.

[7]) H. KAMERLINGH ONNES and G. H. FABIUS, Comm. No. 98.

[8]) E. CARDOSO, Arch. sc. phys. et nat. Genève (4). 34. (1912), pg. 127.

Previously ¹) the value 3.283 was obtained for the critical coefficient on taking $K_{4d} = K_{4s}$; we now find

$$K_{4d} = 3.424$$

which is therefore slightly greater than that for oxygen ²) (3.346). If, therefore, we leave $K_{4d} = 3.13$ for helium out of account, oxygen, and not argon, is the substance for which K_{4d} lies nearest the theoretical value, 2.67, deduced from VAN DER WAALS's equation.

The density of the liquid at — 183°.15 agrees well with the figures given by BALY and DONNAN ³). The difference is less than 1 %.

Although the deviations of the diameter from rectilinearity are sufficiently small to enable one to say that argon obeys the law of the diameter, they are still too large, and especially too systematic, to be due to experimental errors. As is easily seen from the table and from the accompanying figure, the experimental diameter in the neighbourhood of the critical point exhibits a curvature concave towards the axis of temperature, while at higher temperatures it is convex towards the same axis. The same behaviour has already been observed in other substances, e. g. carbon dioxide ⁴).

In fig. 3 are given the reduced density curves and diameters for ether (RAMSAY and YOUNG ⁵)), isopentane (YOUNG ⁶)), oxygen (MATHIAS and KAMERLINGH ONNES ⁷)), xenon (PATTERSON, CRIPPS and WHYTLAW-GRAY ⁸)), argon and helium (KAMERLINGH ONNES ⁹)); the reduction from the experimental data has been made by means of the critical density obtained from the diameter.

On a previous occasion it was shown by KAMERLINGH ONNES and KEESOM ¹⁰) how the equations of state for different substances

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¹) H. KAMERLINGH ONNES and C. A. CROMMELIN, Comm. No. 120*a*.

²) E. MATHIAS and H. KAMERLINGH ONNES, Comm. No. 117.

³) E. C. C. BALY and F. G. DONNAN, Journ. Chem. Soc. Trans. 81. (1912). pg. 911.

⁴) H. KAMERLINGH ONNES and W. H. KEESOM, Comm. No. 104*a*. J. P. KUENEN and W. G. ROBSON, Phil. Mag. (6) 3. (1902) pg. 624.

⁵) W. RAMSAY and S. YOUNG, Phil. Trans. 178. (1887), pg. 57.

⁶) S. YOUNG, Proc. phys. Soc. London, 1894/1895, pg. 602.

⁷) l. c.

⁸) l. c.

⁹) H. KAMERLINGH ONNES, Comm. No. 124*b*

¹⁰) H. KAMERLINGH ONNES and W. H. KEESOM, Enc. Math. Wiss. V. 10. Suppl. N⁰. 23.

Erratum Communication N⁰. 131*a*.

p. 12 line 17 from the top: for higher read lower.

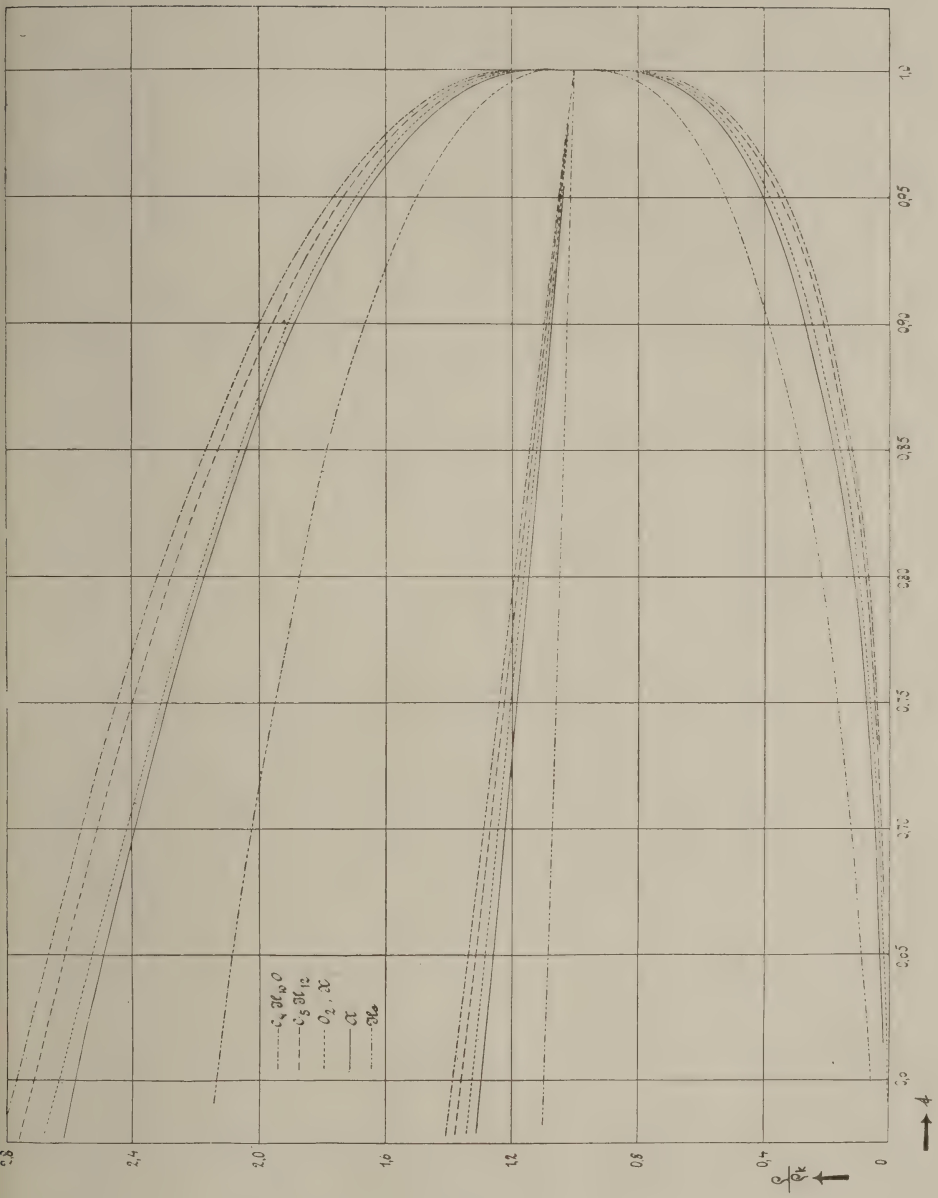

Fig. 3.

deviate one from another, and how these differences may find expression in deviation functions. On doing this, it appears that substances may be arranged in order so that the deviations of successive substances gradually increase, while it also appears that substances of widely divergent critical temperatures are then found to be in the order of their critical temperatures. The exemplification of this general property afforded by the behaviour of the diameter was noticed by one of us some time ago [1]) and is brought to light in fig. 3 in which the density curves are seen to enclose one another.

If the law of corresponding states were strictly obeyed, then these curves ought to coincide exactly. From the diagram, however, it is seen that this is not the case. The curves enclose one another [2]) in such a way that a complex molecular structure and a high critical temperature (circumstances which are usually coexistent) cause divergence between the branches of the curve, while simple molecular structure and a low critical temperature appear to cause them to contract.

Looked at from this point of view it is of importance to note that the curves for xenon and oxygen so closely correspond that there appears no appreciable difference between the density curves in the diagram, and they have accordingly been represented by a single curve. (The observations for xenon, however, extend only to $t = 0.7$). The cause of this correspondence can well be explained on the assumption [3]) that the contracting influence of the simpler molecule and the diverging influence of the comparatively high critical temperature (+ 16°.6 C.) have, at least in part, cancelled each other.

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[1]) E. Mathias, C. R. 139, (1904), pg. 359.

[2]) In the diagram of Nr. 36 of Enc. Math. Wiss. V. 10, Suppl. No. 23, is clearly shown the surrounding of the boundary curve for helium by that for isopentane.

[3]) See Nr. 34*e* of Enc. Math. Wiss. V. 10, Suppl. No. 23.

COMMUNICATIONS

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 131b.

◆

C. A. CROMMELIN. On the triple point of methane.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akademie van Wetenschappen te Amsterdam*, **26 October 1912**, p. 684—685).

EDUARD IJDO — PRINTER — LEIDEN.

C. A. CROMMELIN. *On the triple point of methane.*

The measurements made by Prof. MATHIAS, Prof. KAMERLINGH ONNES and myself on the diameter for argon [1]) afforded an opportunity of determining the pressure and temperature of methane at its triplepoint. For, when the cryostat was filled with liquid methane, and the pressure was reduced so as to give a temperature of about — 183° C. the methane was covered with a solid crust. A slight increase of the pressure caused the solid methane to spread itself in small pieces throughout the liquid. While these pieces were kept in constant motion through the liquid by means of the stirrer, the following triplepoint constants were observed:

$$t = - 183.^\circ 15 \text{ K.} \qquad p = 7.0 \text{ cm.}$$

On account of the manner in which these figures have been determined they must be considered to be very accurate.

As far as I am aware there has hitherto been only one other determination of these data, that of OLSZEWSKI [2]), who found

$$t = - 185.^\circ 8 \text{ and } p = 8.0 \text{ cm.}$$

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[1]) Comm. No. 131*a*.

[2]) K. OLSZEWSKI, C. R. 100, page 940, 1885.

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H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 131c.

H. KAMERLINGH ONNES and **C. A. CROMMELIN.**
Isotherms of monatomic substances and of their binary mixtures. XIV. Calculation of some thermal quantities for argon.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **30 November 1912**, p. 873—881).

Eduard IJdo — Printer — Leiden.

H. KAMERLINGH ONNES and C. A. CROMMELIN. *Isotherms of monatomic substances and of their binary mixtures.* XIV. *Calculation of some thermal quantities for argon.*

The empirical reduced equation of state for argon, VII. A. 3, published some time ago [1]) enables us to calculate a number of thermal quantities, which are essential to a knowledge of monatomic substances in general and of argon in particular. These quantities may also be obtained graphically. Calculation by means of an equation which fits the experimental results over the whole region of observation allows, however, a much greater accuracy to be attained.

In the present paper [2]) we give values of

$$\left(\frac{\partial p}{\partial T}\right)_v, \quad \left(\frac{\partial^2 p}{\partial T^2}\right)_v, \quad \left(\frac{\partial \gamma_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v, \quad \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p,$$

AMAGAT's „pression intérieure" [3]), and of REINGANUM's a,

$$a_R = \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]v^2$$

calculated as functions of the temperature and of the density from equation VII. A. 3 [4]). The temperature is expressed in KELVIN degrees and is calculated from 0° C; the pressure is expressed in international atmospheres [5]).

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[1]) H. KAMERLINGH ONNES and C. A. CROMMELIN. Comm No 128.

[2]) Already indicated in H. KAMERLINGH ONNES and W. H. KEESOM, Suppl. No 23, note 492, p. 146. Preliminary values obtained by C. A. CROMMELIN for some of the quantities here discussed have already been published by E. H. AMAGAT, C. R. 9 April 1912.

[3]) E. H. AMAGAT, numerous papers in the C. R. collected in „Notes sur la Physique et la Thermodynamique." Paris 1912.

[4]) For the notations used in this paper see H. KAMERLINGH ONNES and W. H. KEESOM, Enc. Math. Wiss. V. 10, Suppl. No. 23.

[5]) Enc. math. wiss. V. 10, Suppl. No. 23, Einheiten. *a*.

TABLE I.

$\left(\frac{\partial p}{\partial T}\right)_v$.

ρ_N	+ 20°	0°	— 20°	— 40°	— 60°	— 70°	— 80°	— 90°	— 100°	— 110°	— 113°	— 116°	— 119°	— 122°
20	+0.0764	+0.0766	+0.0768	+0.0770	+0.0773	+0.0775	+0.0777	+0.0779	+0.0781	+0.0784	+0.0785	+0.0786	+0.0787	+0.0788
40	1589	1595	1603	1612	1624	1630	1638	1646	1655	1665	1669	1672	1676	1680
60	2471	2485	2501	2521	2545	2559	2575	2593	2614	2637	2644	2652	2660	2668
80	3409	3431	3457	3490	3531	3556	3584	3615	3650	3690	3703	3717	3731	3745
100				4517	4578	4615	4657	4704	4759	4821	4841	4861	4883	4904
120							5790	5857	5934	6022	6051	6080	6110	6141
140									7173	7292	7331	7371	7411	7453
160									8473	8627	8678	8730	8783	8837
180										1.0030	1.0093	1.0159	1.0227	1.0296
200											1580	1662	1747	1833
220											3142	3243	3348	3455
240												4913	5041	5172
260												6683	6839	6998
280												8568	8757	8951
300												2.0589	2.0817	2.1053
320												2769	3044	3329
340												5136	5467	5810

TABLE II.

$\left(\frac{\partial^2 p}{\partial T^2}\right)_v$

ρ_N	+20°	0°	—20°	—40°	—60°	—70°	—80°	—90°	—100°	—110°	—113°	—116°	—119°	—122°
20	—0.00001	—0.00001	—0.00002	—0.00001	—0.00002	—0.00001	—0.00003	—0.00002	—0.00002	—0.00003	—0.00002	—0.00003	—0.00003	—0 00003
40	3	3	4	3	6	6	8	9	10	11	11	12	12	13
60	6	7	9	10	14	15	17	19	21	24	26	26	27	28
80	10	12	15	18	24	25	30	35	37	43	43	46	47	48
100				27	35	39	44	51	58	66	68	69	72	74
120							63	73	82	93	97	100	102	106
140									111	126	130	135	138	141
160									144	165	171	175	179	182
180										210	216	223	228	232
200											271	279	285	288
220											334	344	353	358
240												420	432	438
260												512	526	536
280												620	640	653
300												748	775	795
320												899	935	963
340												1079	1125	1165

TABLE III.

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

ρ_N	+ 20°	0°	— 20°	— 40°	— 60°	— 70°	— 80°	— 90°	— 100°	— 110°	— 113°	— 116°	— 119°	— 122°
20	+ 1.150	+ 1.198	+ 1.254	+ 1.314	+ 1.381	+ 1.417	+ 1.454	+ 1.494	+ 1.533	+ 1.579	+ 1.593	+ 1.604	+ 1.620	+ 1.635
40	4.525	4.703	4.905	5.134	5.388	5.523	5.670	5.826	5.990	6.163	6.218	6.273	6.331	6.387
60	9.996	10.37	10.79	11.27	11.82	12.12	12.43	12.77	13.14	13.52	13.64	13.76	13.89	14.01
80	17.44	18.05	18.75	19.55	20.46	20.98	21.53	22.11	22.74	23.42	23.63	24.84	24.06	24.27
100				29.79	31.15	31.92	32.75	33.65	34.62	35.65	35.98	36.31	36.64	36.97
120							45.91	47.18	48.55	50.03	50.49	50.95	51.42	51.90
140									64.38	66 38	67.00	67.63	68.27	68.90
160									81.94	84.54	85.35	86 18	87.00	87.83
180										104.4	105.4	106 5	107.6	108.6
200											127.2	128.5	129.8	131.1
220											150.5	152.2	153.8	155.4
240												177.4	179.4	181.4
260												204.4	206.9	209.3
280												233.2	236.1	239.1
300												263.8	267.4	270.9
320												296.5	300.7	305.1
340												331.3	336.4	341.7

TABLE IV.

$$a_{RN} = \left\{ T\left(\frac{\partial p}{\partial T}\right)_v - p \right\} v_N^2$$

ρ_N	+ 20°	0°	— 20°	— 40°	— 60°	— 70°	— 80°	— 90°	— 100°	— 110°	— 113°	— 116°	— 119°	— 122°
20	+0.002875	+0.002996	+0.003134	+0.003285	+0.003453	+0.003541	+0 003636	+0.003735	+0.003833	+0.003946	+0.003983	+0.004011	+0.004050	+0.004088
40	2828	2940	3066	3208	3367	3452	3543	3641	3743	3852	3886	3921	3957	3992
60	2777	2880	2997	3131	3282	3366	3454	3548	3649	3756	3789	3823	3857	3893
80	2725	2821	2930	3054	3197	3278	3363	3455	3554	3659	3692	3725	3759	3793
100				2979	3115	3192	3275	3365	3462	3565	3598	3631	3664	3697
120							3188	3276	3372	3474	3506	3539	3571	3604
140									3285	3387	3418	3451	3483	3516
160									3201	3302	3334	3366	3399	3431
180										3223	3255	3287	3319	3352
200											3180	3212	3245	3278
220											3110	3144	3177	3211
240												3081	3115	3150
260												3024	3060	3096
280												2974	3012	3050
300												2931	2971	3011
320												2895	2937	2979
340												2866	2910	2956

TABLE V.

$$\left(\frac{\partial \gamma_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

ρ_N	+ 20°	0°	— 20°	— 40°	— 60°	— 70°	— 80°	— 90°	— 100°	— 110°	— 113°	— 116°	— 119°	— 122°
20	— 0.00293	— 0 00273	— 0.00506	— 0 00233	— 0.00426	— 0.00203	— 0.00579	— 0.00366	— 0.00346	— 0.00489	— 0.00320	— 0.00471	— 0.00462	— 0.00453
40	879	819	1012	699	1279	1219	1543	1648	1731	1794	1761	1885	1849	1964
60	1759	1912	2278	2331	2983	3046	3283	3479	3635	3914	4162	4084	4160	4231
80	2931	3277	3796	4196	5114	5077	5793	6408	6404	7013	6884	7226	7242	7252
100				6293	7458	7921	8496	9338	0.10039	0.10764	0.10886	0.10839	0.11094	0.11181
120							0.12165	0.13366	14193	15167	15529	15709	15717	16016
140									19213	20549	20812	21207	21264	21304
160									24925	26910	27375	27491	27582	27498
180										34249	34579	35031	35133	35053
200											43384	43828	43916	43514
220											53470	54039	54394	54090
240												65978	66567	66177
260												80430	81051	80984
280												97396	98618	98662
300												1.1750	1.1942	1.2012
320												1.4122	1.4407	1.4550
340												1.6950	1.7335	1.7602

The importance of a knowledge of these quantities especially as functions of the temperature has already been repeatedly insisted upon [1] so that we need say nothing further here upon that point. We shall only say that according to the chief VAN DER WAALS equation with constant a_W, b_W and R_W, $\left(\frac{\partial p}{\partial T}\right)_v$, $\left(\frac{\partial u}{\partial v}\right)_T$ and a_R should be independent of the temperature, and consequently $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$ should vanish, so that the deviations which they all show may be taken as a measure of the degree to which argon deviates from the simple assumptions regarding molecules accepted by VAN DER WAALS in developing his principal equation.

Agreement, at least approximate, with the chief VAN DER WAALS equation would first be expected in the monatomic substances, and therefore the investigation of these quantities for argon as well as a comparison of the results with those for substances of more complex molecular structure is of the greatest importance.

Consideration of the quantity introduced by REINGANUM [2]

$$a_R = v^2\left[\,T\left(\frac{\partial p}{\partial T}\right)_v - p\,\right] = -\left(\frac{\partial u}{\partial \rho}\right)_T$$

enables us to see that, as far as the mutual actions of the molecules is concerned, the assumptions upon which VAN DER WAALS founded his chief equation with constant a_W, b_W and R_W must undergo some modification such as has recently been introduced by VAN DER WAALS in the various developments of the consideration of apparent association. If we retain for the moment the most immediate assumption suitable for monatomic substances such as argon, that the atoms are incompressible, then changes in a_R would be wholly due to deviations of the molecular forces from the simple initial assumptions made by VAN DER WAALS. Such changes in a_R might originate from three causes: change in the a_W, in the b_W, or in the R_W of the chief equation, as a result of the radius of the sphere of action being but slightly greater than that of the molecule, a circumstance revealed in apparent association [1]).

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[1] M. REINGANUM, Diss. Göttingen 1899, Ann. d. Phys. (4) 18 (1905), p. 1008. Suppl. No 23, p. 140 sqq.

[2] l. c.

Since $$T\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \left(\frac{\partial \gamma_v}{\partial v}\right)_T$$

the question as to whether $\left(\frac{\partial p}{\partial T}\right)_v$ is independent of the temperature and therefore $\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$, is most intimately connected with the question as to whether $\left(\frac{\partial \gamma_v}{\partial v}\right)_T = 0$ or not. For a long time this question remained undecided on account of the lack of experimental data. We now know that, at least for a number of substances, $\left(\frac{\partial p}{\partial T}\right)_v$ is in general a function of the temperature, and that therefore $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$ does not vanish.

If we now compare the behaviour of argon with respect to $\left(\frac{\partial p}{\partial T}\right)_v$ with that of isopentane we find correspondence in many respects. YOUNG deduced from his observations upon isopentane that $\left(\frac{\partial p}{\partial T}\right)_v$ decreases with falling temperature for $v_\Gamma < 4.6$ c.c. At greater volumes up to $v_\Gamma = 400$ c.c. it increases with falling temperature while it remains practically constant at still greater volumes. For argon, for which the volumes are expressed in terms of the normal volume as unit, if the law of corresponding states were accurately obeyed, these volumes would correspond to $v_N = 0.00377$ and $v_N = 0.328$ or $\rho_N = 265$ and $\rho_N = 3.05$. The argon observations embraced by VII. A. 3. lie entirely within these limits, and from Table I we see that argon agrees with isopentane within the region of observation. Over the entire region $\left(\frac{\partial p}{\partial T}\right)_v$ falls with increasing temperature. At the lowest argon density $\rho_N = 20$ the diminution becomes extremely small, pointing to constancy at still lower densities. Argon differs from isopentane, however, in this respect that with argon at higher densities far above $\rho_N = 265$, the increase becomes still more rapid, while the behaviour of isopentane would lead one to expect a diminution in the rate of increase.

---

[1] This circumstance causes a change in b_W also, cf. H. KAMERLINGH ONNES and W. H. KEESOM, Suppl. No. 23, Nr. 47.

From his observations upon isopentane YOUNG deduced the following rule for the behaviour of $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$:

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_{v < \pm v_k} > 0 ; \left(\frac{\partial^2 p}{\partial T^2}\right)_{v > \pm v_k} < 0.$$

This rule has already been confirmed for a variety of substances, and is, as far as its second part is concerned, also obeyed by argon.

For carbon dioxide, ethylene and isopentane, REINGANUM found that the quantity $a_R = \left[T \left(\frac{\partial p}{\partial T}\right)_v - p \right] v^2$ is a minimum for v about $\frac{8}{4} v_k$, and at a temperature about 10 degrees above t_k. If the law of corresponding states were strictly true this minimum for argon should be at $\rho_N = 380$, and therefore outside the region of experiment. Nothing can be done consequently beyond trying to judge from extrapolation, if, and where, the minimum exists

If for this purpose we graph a_R as a function of ρ_N at —122° and —116°, then extrapolation towards higher densities shows that it is probable that these curves would exhibit a minimum for argon also at $v = \frac{3}{4} v_k$.

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* * *

H. KAMERLINGH ONNES and BENGT BECKMAN. On the HALL effect, and on the change in resistance in a magnetic field at low temperatures. VI. The HALL effect for nickel, and the magnetic change in the resistance of nickel, mercury and iron at low temperatures down to the melting point of hydrogen.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akademie van Wetenschappen te Amsterdam*, **30 November 1912**, p. 881—887.)

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and BENGT BECKMAN. *On the* HALL *effect, and on the change in resistance in a magnetic field at low temperatures.* VI. *The* HALL *effect for nickel, and the magnetic change in the resistance of nickel, mercury and iron at low temperatures down to the melting point of hydrogen.*

§ 17 [1]. *Magnetic change in the resistance of solid mercury.* The resistance was measured of mercury contained in a glass capillary 9 cms. long, and 0.12 mm. diameter. The capillary was U-shaped, and to either end were fused two glass leading tubes which were filled with mercury. The resistances were measured by the KOHLRAUSCH method of overlapping shunts, in which the main current was $I = 0.006$ amp. The mercury was frozen by blowing cooled hydrogen vapour into the cryostat through a glass tube whose lower extremity reached below the resistance. The resistance was found to be

7.97 Ω	at	$T = 287^\circ.3$ K.
0.1014		$20^\circ.3$
0.0618		$14^\circ.5$

TABLE XIX.

Magnetic change in the resistance of mercury.

$T = 20^0.3$ K.		$T = 14^0.5$ K.	
H in gauss.	$\frac{\Delta w}{w} \times 10^3$	H	$\frac{\Delta w}{w} \times 10^3$
9760	+ 1.3	10270	+ 5.5
10270	+ 1.5	10270	+ 6.5
10270	+ 1.6		

---

[1] The sections of this paper are numbered in continuation of those of Comm. N⁰. 130*c* (Oct. 26, 1912).

The measurements therefore show an increase of the resistance in the magnetic field.

$$\text{At } H = 10000 \text{ and } T = 20^\circ 3 \text{ K.} \quad \frac{\Delta w}{w} = + 1.5 \times 10^{-3}$$

$$T = 14^\circ 5 \text{ K.} \quad \frac{\Delta w}{w} = + \ 6 \times 10^{-3}$$

were obtained as mean values.

At these temperatures the temperature coefficient of the resistance is very great, and this lessens the accuracy of the above measurements, especially at $T = 14^\circ.5$ K. The large increase occasioned by lowering the temperature from 20° to 14° K is very striking.

§ 18. *The* Hall *effect for, and the magnetic change in the resistance of, nickel.* The material in the form of a plate of 0.053 mm. thickness was pure Schwerte nickel. H and RH are given in c. g. s. units. I was 0.7 to 0.9 amp.

TABLE XX.

Hall effect for Nickel, Ni_{pl}.

$T = 290^0.5$ K.			$T = 90^0$ K.			$T = 20^0.3$ K.			$T = 14^0.5$ K.		
H	RH	$-R \times 10^4$	H	RH	$-R \times 10^4$	H	RH	$-R \times 10^4$	H	RH	$-R \times 10^4$
3010	18.8	62.4	2980	2.93	9.83	2970	1.48	4 98	4940	2.50	5.06
5170	31.2	60.3	4950	4.58	9.25	5640	2.86	5.08	8250	4.25	5.15
7260	39.3	54.1	7290	6.31	8 65	7260	3.53	4.86	10270	5.19	5.05
9065	43.1	47.6	9110	7.62	8.36	8250	4.08	4.95			
10270	44.9	43 7	10400	8 29	7.98	10270	4.81	4.68			

The results given in Table XX are shown graphically in Figs. 1 and 2.

The Hall effect for nickel decreases as the temperature falls from ordinary room temperature; this has already been found by A. W. Smith [1]) to be the case down to liquid air temperatures. According to A. Kundt [1]) the Hall effect for ferro-magnetic substances is proportional to the magnetisation and not to the field. Hence, when the magnetisation attains its maximum value, the Hall effect must also exhibit a state of saturation, that is to say, the curves giving the Hall effect as a function of the field must show a bend. Smith's curves, covering a region of temperature from — 193° C. to + 546° C., show such a bend, which, as the temperature increases right up to the critical temperature for nickel, is displaced towards the weaker fields, thus corresponding to a diminution of the saturation magnetisation as the temperature rises. At 290° K. our present measurements show this bend clearly at about 5000 to 6000 gauss. At the lower temperatures there is no decided bend visible within the region of fields covered by our observations ($H < 10400$); thus if there are any bends at these temperatures, they must occur at still stronger fields.

---

[1]) A. W. Smith: Phys. Rev. **30**, 1, 1910.

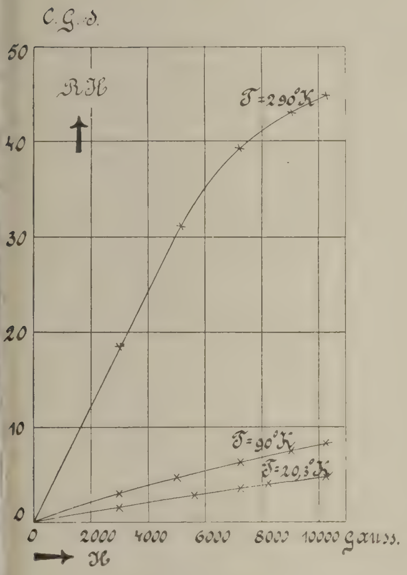

Fig. 1.

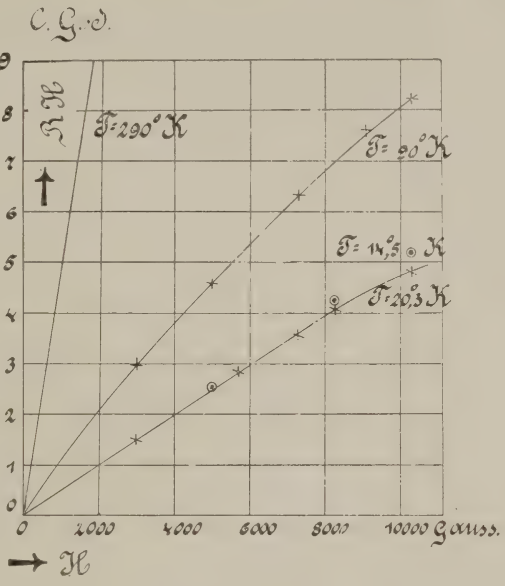

Fig. 2.

At 14°.5 K. the Hall effect is strictly proportional to the field, as is also the case at 20°.3 K. as far as $H = 9060$. At 90° K. the HALL coefficient is a linear function of the field, diminishing as the field increases.

---

[1]) A. Kundt: Wied. Ann. **49**, 257, 1893.

For the HALL coefficient in very weak fields the relation

$$R_0 = c\,e^{bT}$$

holds.

The LEDUC quantity $D_L = \frac{R}{w}$, the tangent of the angle of rotation of the equipotential lines in unit field, is here a linear function of the temperature.

The following Table shows the extent to which those relations hold.

TABLE XXI.

R_0 and D_L as functions of the temperature.

T	$R_{0\,obs.}$	$R_{0\,calc.}$	$D_{L\,calc.}$	$D_{L\,obs.}$
290° K.	66.0×10^{-4}	67.5×10^{-4}	5.37	5.37
90	11.2	10.5	3.07	3.10
20.3	5.0	5.3	2.22	2.30
(14.5	5.1	5.0	2.28	2.22)

For the nickel plate the magnetic change of resistance was also measured. I was 0.2 to 0.3 amp.

TABLE XXII.

Change in the resistance of nickel in a magnetic field.

$T = 290°.5$ K.		$T = 90°$ K.		$T = 20°.3$ K.		$T = 14°.5$ K.	
H	$\frac{\Delta w}{w} \times 10^3$	H	$\frac{\Delta w}{w} \times 10^3$	H	$\frac{\Delta w}{w} \times 10^3$	H	$\frac{\Delta w}{w} \times 10^3$
1750	+ 0.5	2270	+ 2	1750	+ 1	2970	0
2500	+ 0.5	2520	+ 3	2520	+ 2	5640	− 7
2970	0	3770	0	3750	0	8250	− 11
3750	− 2	4950	− 5.5	5640	− 8	10270	− 13
5170	− 4	6140	− 6.5	8250	− 12		
7260	− 7	8290	− 9.5	9065	− 13		
9065	− 9	9110	− 12.5	10270	− 15		
10270	− 11	10400	− 14.0				
0	$w = 12.2 \times 10^{-4}\,\Omega$	0	$w = 3.63 \times 10^{-4}\,\Omega$	0	$w = 2.25 \times 10^{-4}\,\Omega$	0	$w = 2.23 \times 10^{-4}\,\Omega$

As the resistance of the plate is very small, and the changes were, at the most, 1.5 %, it was not possible to evaluate them with any greater accuracy.

As has also been observed by F. C. Blake[1]), G. Barlow[2]) and C. W. Heap[3]), there is an increase in the resistance of nickel in the weaker fields ($H < 3000$); in stronger fields the resistance diminishes, and, in the region $5600 < H < 10270$, does so approximately linearly with the field. This behaviour is, to a large extent, the same throughout the region 290° K. $> T >$ 14°.5 K.

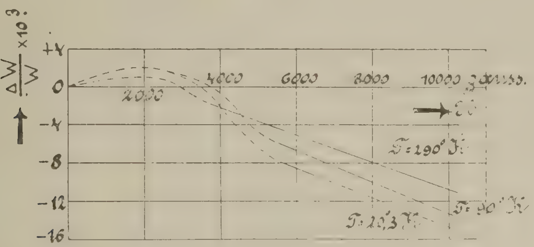

Fig. 3.

In strong fields the diminution in the resistance is somewhat greater at low temperatures than at ordinary temperature.

§ 19. *Change in the resistance of pure iron in a magnetic field.* As experimental material an iron wire from Kohlswa, Sweden, was used for which we are indebted to the kindness of Prof. C. Benedicks, Stockholm. On analysis the following impurities were found present

C	0.10 %
S	0.007
P	0.028
Si	0.014
Mn	0.03

thus giving a total impurity of about 0.18 %. After analysis the wire was drawn by Heraeus to a diameter of 0.1 mm.

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[1]) F. C. Blake. Ann. d. Phys. **28**, 449, 1909.

[2]) G. Barlow. Proc. Roy. Soc. **71**, 30, 1903.

[3]) C. W. Heap. Phil. Mag. (6) **22**, 900, 1911.

Before it was drawn the temperature coefficient was

$$\frac{w_{80^\circ}}{w_{289^\circ}} = 0.14\,;$$

afterwards was

$$\frac{w_{80^\circ}}{w_{289^\circ}} = 0.17\,.$$

The iron wire was wound non-inductively upon an ebonite cylinder, and was so placed in the magnetic field as to be perpendicular to the lines of force throughout. The method of overlapping shunts was used for determining the resistance. Resistances without field are given in Table XXIII.

TABLE XXIII.
Resistance of pure iron as a function of the temperature.

T	w
288°.0 K.	11.18 Ω
90	2.225
77.5	1.859
20.3	1.129
14.5	1.124

The temperature coefficient of the resistance is very small in the liquid hydrogen region; in liquid oxygen and nitrogen it is large. Resistances were measured at 288° K., 77° K, 20°.3 K. and 14°.5 K. The measurements at 77° K. are not quite trustworthy, and we communicate them only because they are sufficiently accurate to determine the orientation of the temperature curve.

Fig. 4 shows the resistance as a function of the field. The observations at 77° K. are indicated by a broken line.

At 288° K. the resistance increases in weak fields, and decreases in fields greater than 7000. This is in agreement with results obtained by L. Grunmach and F. Weidert [1]), C. W. Heap [2]), and others. At liquid hydrogen temperatures this behaviour is reversed, for the resistance diminishes in weaker fields and increases when $H > 7000$. There is a neutral zone at about $H = 7000$.

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[1]) L. Grunmach and F. Weidert: Verh. d. Deutsch. Physik. Ges. 1906, 359.

[2]) C. W. Heap: l. c.

TABLE XXIV.

Magnetic change in the resistance of iron.

$T = 288^\circ$ K.		$T = 20^\circ.3$ K.		$T = 14^\circ.5$ K.	
H	$\frac{\Delta w}{w} \times 10^4$	H	$\frac{\Delta w}{w} \times 10^4$	H	$\frac{\Delta w}{w} \times 10^4$
990	+ 2.8	1500	— 2.0	990	— 1.7
1500	+ 3.8	2520	— 2.9	2500	— 2.6
2520	+ 5.7	3750	— 2.7	3750	— 3.1
3750	+ 6.0	4940	— 2.2	4940	— 2.4
4940	+ 5.4	6110	— 0.9	6110	— 1.4
6110	+ 3.2	7260	+ 0.7	7260	+ 0.3
7260	+ 0.3	8250	+ 2.6	8250	+ 2.6
8260	— 2.1	9065	+ 3.6	9065	+ 3.6
9065	— 4.7	9750	+ 4.6	9750	+ 4.7
10270	— 9.1	10270	+ 5.2	10270	+ 5.4

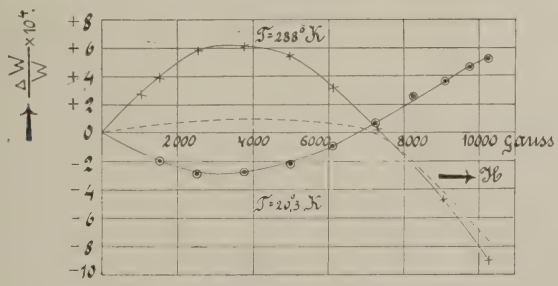

Fig. 4.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory

N°. 132^b.

* * *

H. KAMERLINGH ONNES and **BENGT BECKMAN.**

On the change induced by pressure in electrical resistance at low temperatures. I. Lead.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **30 November 1912**, p. 888—893).

EDUARD IJDO. — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and BENGT BECKMAN. *On the change induced by pressure in electrical resistance at low temperature.* I. *Lead.*

§ 1. *Introduction.* The difficulties which encompass the explanation of the variation of resistance with temperature on the lines of the theory of electrons as developed by RIECKE, DRUDE and LORENTZ, and are of particular import within the region of low temperatures, render it desirable to undertake an investigation of the behaviour of resistance at these temperatures under modification of various external conditions. With that end in view we have already developed in certain directions an investigation of the behaviour of resistance in a magnetic field (and of the closely allied HALL phenomenon) In the present paper we communicate the result of a first investigation of the change of resistance under the influence of uniform hydrostatical pressure. Our first aim had been to trace the connection between pressure coefficient and temperature coefficient. Our data, however, are as yet too few to serve as a basis for deductions — however obvious these may be — affording an explanation by means of vibrators, electrons, dissociation or variation of the mean speed [1]).

The dependence of specific resistance (w_{sp}) upon pressure (p) can, in general, be represented by the formula [2])

$$w_{sp} = w_{1sp} \; e^{-ap-bp^2}$$

in which a and b are constants, and w_{1sp} is the specific resistance for $p=1$. When p is not very great, this gives

$$w = w_1 \,(1 - ap)\,(1 + \tfrac{1}{3}\beta p) = w_1\,(1 + \gamma p)$$

for the resistance of a wire which is subjected to uniform hydrostatical pressure, in which

$$-\gamma = a - \tfrac{1}{3}\beta$$

and β is the compressibility. Hence the variation $\Delta w = w - w_1$, is given by $\dfrac{\Delta w}{w} = \gamma p$.

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[1]) B. BECKMAN: Upsala Univ. Årsskrift 1911 p. 107.

[2]) B. BECKMAN: l. c p. 16.

In the following only γ has been measured.

The measurement of γ at very low temperatures is one of extreme difficulty. For, at these temperatures, the temperature coefficient is so great that even the smallest fluctuations of temperature can greatly affect the resistance; in this way a slight disturbance of the temperature equilibrium can occasion a variation of the resistance which completely obscures the whole phenomenon of variation with pressure With the wire we used, for instance, at $T = 20°.3$ K. a pressure of 100 atm. brought about a change in the resistance of only about 0.001Ω, while a change of 0.0003Ω was the result of a variation of 0°.01 in the temperature. And it is pretty obvious that it is a matter of extreme difficulty to re-adjust the temperature to within 0°.01 of its former value after it has been altered by the heating or cooling of the liquid occasioned by fluctuations in the pressure.

There is a second factor operating which renders the measurement difficult. When the compression has been continued for a long time, elastic after effects occur which can also attain a value that is a considerable fraction of the magnitude to be observed. Should, therefore, the variation of pressure be distributed over a long period of time in order to disturb the temperature equilibrium as little as possible, this after action will give rise to a source of error.

§ 2. The lead to be subjected to pressure consisted of a turning about 2 metres long and about 0.2 mm. in diameter. After some practice these long thin turnings could be successfully prepared. Attempts to draw wires of this small cross-section did not meet with success. The wire, a, was wound upon an ebonite cylinder (see fig. 1). To either end was soldered a band, c_1, c_2, rolled from a wire of electrolytic copper; to these bands were soldered the two pairs of leads, d_1, d_2, d_3, d_4. To enable one to subject the lead to pressure it was enclosed in a thick-walled copper cylinder, A_1, closed below by a heavy cap, A_2, (screwed and soldered), and above by a cap A_3 through which two copper capillaries A_4, A_5, pass. One of these capillaries, A_4, is used for filling the cylinder with liquefied gas and for exerting pressure upon the liquid, while the other, A_5, is connected to a manometer and, at the same time, acts as a safety valve, in allowing the liquefied gas to escape in the event of the supply tube getting frozen. This second tube also admits the wires required for the resistance measurements. At the upper end of A_5 these wires pass through a perforated cylinder of ebonite in which they are cemented with marine glue, and this cylinder is held tight against the tube by a screw cap. Resistances were measured by the method of overlapping shunts.

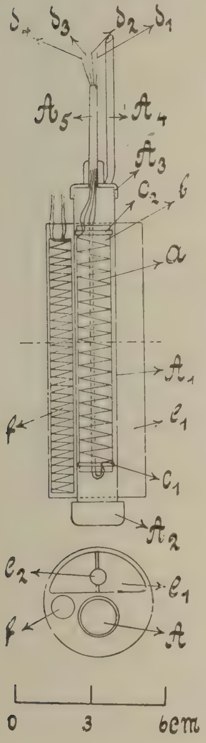

Fig. 1.

The cylinder was immersed in a cryostat, Cr, consisting of a transparent vacuum glass provided with a pump stirrer (see fig. 2). Fig. 1 shows the latter in aspect and cross section. c_1 is the cylinder and c_2 the piston. The temperature of the bath was regulated and measured by means of the gold resistance thermometer f, also shown in fig. 1. We may refer to earlier diagrams (Comm. No. 83, Pl. IV, and Comm. No. 127, p. 23) in which the same letters have been used, for details of the arrangement Y_{30}, Y_{31}, Xa, Xb, X_{90}, X_{91}, Y'_4, for regulating the pressure under which the liquid in the cryostat vaporises.

When the temperature of the cryostat has been adjusted the same kind of gas as has been liquefied in it is admitted into the experimental cylinder by the tap K_1 through A_4 from the reservoir R_{1a} which has previously been filled at high pressure. A second reservoir R_{1b} is coupled in parallel with R_{1a} so that gas need be taken from R_{1a} only in sufficient quantity to complete the filling of the cylinder. In this way the reservoir R_{1a} is much longer available for raising the pressure in the experimental cylinder to the highest values. An other reservoir R_2 served as a regulator, and, as gas was added, the pressure was read on the manometer M_1. The tap K_2 was used for the evacuation of the apparatus and connections before the experiments began. The supply of gas was regulated by K_3. Behind K_3 a cylinder B is coupled in parallel with the experimental tube to serve as a buffer; to the inlet tube of this cylinder is coupled not only the experimental cylinder but also the differential manometer, M_2, to which we shall return just now. Through the tap K_4 gas can be allowed to escape from the experimental cylinder and from the buffer. The pressure of the gas they contain can thus be kept at any desired constant value by means of K_3 and K_4. Regulation of the pressure is made according to the indications of the differential manometer M_2, one side of which is attached to the experimental apparatus and the other to a reservoir R_3 which is maintained at the required constant pressure and is, for that purpose, immersed in ice. To adjust to the desired pressure the differential manometer is first rendered inoperative by opening the tap K_5. Care must be taken in admitting pressure to the manometer that friction does not give rise to difference of pressure between the parts of the apparatus it connects sufficient to cause the mercury of the differential manometer to be blown over. Two steel overflow vessels M_{21}, M_{22}, serve as a safety device. The pressure in the experimental cylinder is read from the manometer M_3, which is connected to A_5. K_6 is a safety valve which comes into operation when A_5 must be used for exhausting.

§ 3. An idea of the degree of purity of the lead is obtained from the values which we give here for the resistance at various temperatures.

TABLE I.

Resistance of the lead wire Pb_{I} at low temperatures.

T	w
289° K.	12.75 Ω
90°	3.77
20°.3	0.725
17°.8	0.626
14°.5	0.520

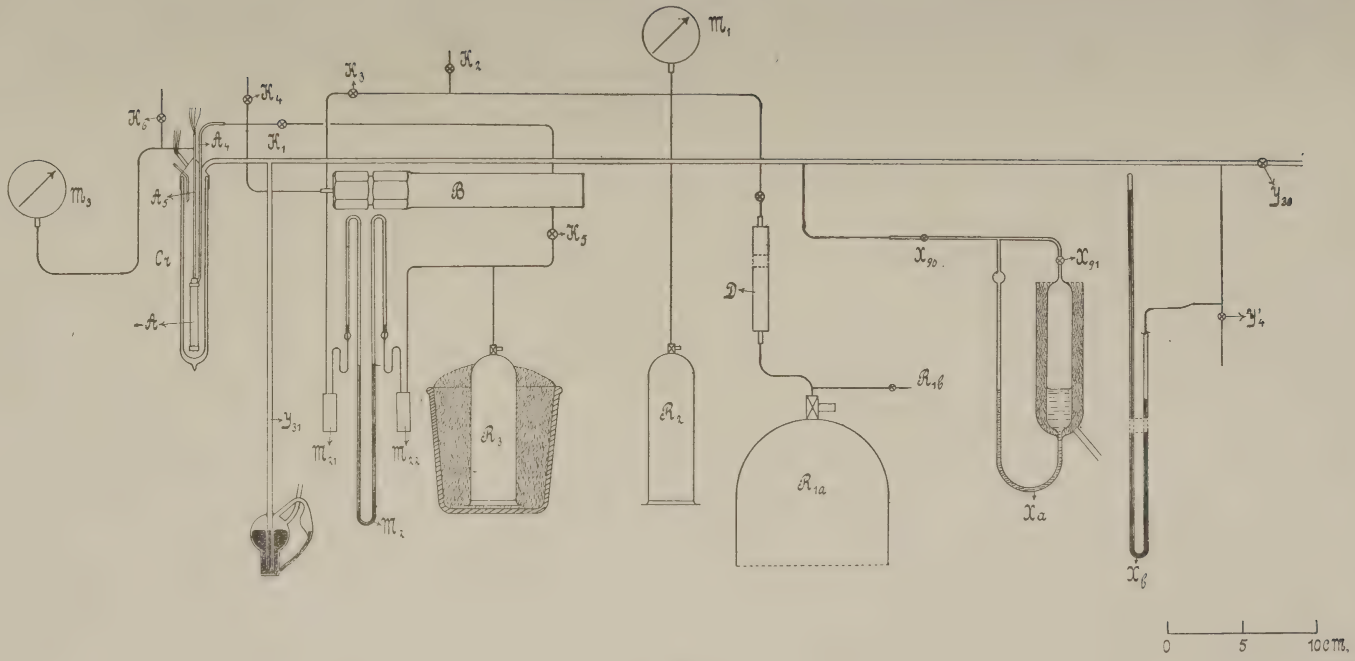
$\mathfrak{M}_1$
$\mathfrak{K}_2$
$\mathfrak{K}_3$
$\mathfrak{K}_4$
$\mathfrak{K}_6$
$\mathfrak{K}_1$
$\mathfrak{A}_4$
$\mathfrak{M}_3$
$\mathfrak{A}_5$
Cr
$\mathfrak{A}$
$\mathfrak{B}$
$\mathfrak{K}_5$
$\mathfrak{Y}_{31}$
$\mathfrak{M}_{21}$
$\mathfrak{M}_{22}$
$\mathfrak{M}_2$
$\mathfrak{R}_3$
$\mathfrak{R}_2$
$\mathfrak{D}$
$\mathfrak{R}_{1b}$
$\mathfrak{R}_{1a}$
$\mathfrak{X}_{90}$
$\mathfrak{X}_{91}$
$\mathfrak{X}_a$
$\mathfrak{X}_b$
$\mathfrak{Y}'_4$
$\mathfrak{Y}_{30}$
0
5
10 cm.

Fig. 2.

Comparison of these values with those given by KAMERLINGH ONNES and CLAY, Comm. No. 99*c*, shows that the lead now used must hold in solid solution a fairly considerable amount of foreign matter, for the great change in the temperature coefficient exhibited by metals in the presence of small amounts of impurity may generally be attributed to the transition of this admixture to a state of solid solution.

Our measurements were made with liquid oxygen and liquid hydrogen as compressing liquids. The results are contained in Table II. The pressure (p) is given in atmospheres.

TABLE II.

Change induced in the resistance of lead, Pb_{I} by compression at low temperatures.

$T = 90°$ K.			$T = 20°.3$ K.		
p	Δw	$\frac{1}{p}\,\frac{\Delta w}{w}$	p	Δw	$\frac{1}{p}\,\frac{\Delta w}{w}$
49.4	— 0.0043 Ω	— 2.35 × 10^{-5}	49.7	— 0.00062	— 1.7 × 10^{-5}
97.8	— 0.0080	— 2.2	97.5	— 0.00114	— 1.6
102.5	— 0.0085	— 2.2	97.5	— 0.00132	— 1.8
48.5	— 0.0040	— 2.3	98	— 0.00115	— 1.6
97	— 0.0079	— 2.2	97.5	— 0.00131	— 1.8
			97.5	— 0.00114	— 1.6

For the pressure coefficient E. LISELL[1]) gives

$$\gamma = -1.44 \,.\, 10^{-5} \quad \text{at} \quad T = 273° \text{ K.}$$

From our measurements we find

$$\gamma = -2.25 \,.\, 10^{-5} \quad \text{at} \quad T = 90° \text{ K.}$$

and

$$\gamma = -1.7 \,.\, 10^{-5} \quad \text{at} \quad T = 20°.3 \text{ K}$$

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[1]) E. LISELL: Upsala Univ. Årsskrift 1903.

so that the pressure coefficient has become somewhat greater at the lower temperatures. The increase obtained between 273° K and 90° K. changes again to a diminution. The accuracy of the measurements is still too small to allow us to attribute any significance to this diminution at the lowest temperatures.

If we consider the decrease $-\Delta w$ in the resistance for $p = 100$ atm., we find that it approximates to zero at the lower temperatures. Thus we find for Pb_{I}:

273° K. for $p = 100$ atm. $-\Delta w = 0.017\ \Omega$

90 K. „ $p = 100$ „ $-\Delta w = 0\ 008$

20,3 K. „ $p = 100$ „ $-\Delta w = 0.001$

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

No. 132c.

BENGT BECKMAN. On the Hall effect, and on the change in resistance in a magnetic field at low temperatures. VII. The Hall effect for gold-silver alloys at temperatures down to the melting point of hydrogen.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **28 December 1912**, p. 1035—1044).

Eduard IJdo. — Printer — Leiden.

BENGT BECKMAN. *On the* HALL *effect, and on the change in resistance in a magnetic field at low temperatures.* VII. *The* HALL *effect for gold-silver alloys at temperatures down to the melting point of hydrogen.*

This Communication is a continuation of Comm. No. 130*b*.

IV. *Gold-silver alloys.*

§ 10. Measurements at temperatures of 290° K., 20°.3 K. and 14°.5 K. of the HALL-effect for three *Au-Ag* alloys (I, II, III) containing a large percentage of gold were published by KAMERLINGH ONNES and myself in Comm. N°. 129*a*, § 12, and in Comm. N°. 130*c*, § 16. The results of my measurements made on one (I) of these alloys at 90° K. were given in § 9 of Comm. N°. 130*b*. I have since investigated three other alloys containing a greater percentage of silver, and in the present paper the results of these new measurements on the HALL-effect for *Au-Ag* alloys are given and are discussed in connection with the former results.

The observational method was the same as was formerly used, viz. the form of the compensation method developed by LEBRET [1]) as used by VAN EVERDINGEN [2]). An iron-clad THOMSON galvanometer was used, with a period of about 4 secs, and a sensitivity of about 1 mm. deflection at 2.5 m. distance for 5×10^{-8} volts. In this method disturbances produced by the thermo-currents arising from the galvanomagnetic difference of temperature of VON ETTINGSHAUSEN are completely eliminated only in the case of instantaneous closing of the main current circuit. On account of the comparatively large period of the galvanometer this was not possible in the present experiments; but still, these disturbances were too small in the present case to be observed.

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[1]) LEBRET. Diss. Leiden 1895. Comm. N°. 19, 1895.

[2]) E. VAN EVERDINGEN, Comm. Leiden, Suppl. N°. 2. Cf. also H. KAMERLINGH ONNES and B. BECKMAN, Comm. N°. 129*a*, 1912.

The main current was 0.5 to 1 amp. The plates were circular (11 mm. diam.) with point electrodes. The resistance of the plates was measured as well as the HALL effect.

The alloys were obtained by fusing pure gold and silver in a porcelain crucible, and then rolling them out. They were all submitted to analysis. I am greatly indebted for these analyses to Dr. C. HOITSEMA, Master of the Royal Mint, Utrecht, and to Fil. Lic. G. KARL ALMSTRÖM, Upsala.

In the Tables, H represents the field strength in gauss, R the HALL coefficient in c. g. s. units, w_T the resistance in ohms at the absolute temperature T, and w_0 the resistance at 0° C.

Alloy II contained 10.7 atomic percentage of silver. The thickness of the plate was 0.049 mm.

TABLE XVI.

HALL effect for $(Au\text{-}Ag)_{II}$

H	$T = 290°$ K.		$T = 90°$ K.	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$
8250	5.25	6.36	4.26	5.16
9360	—	—	4.96	5.31
9750	6.25	6.41	5.08	5.21
10270	6.51	6.34	5.45	5.31
0	$w = 8.06 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 1.03.$		$w = 5.43 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 0.69.$	

Alloy III contained 30 atomic percent of *Ag*. The plate was 0.078 mm. thick.

TABLE XVII.

HALL effect for $(Au\text{-}Ag)_{III}$

$T = 290^\circ$ K.			$T = 90^\circ$ K.		
H	RH	$-R\times10^4$	H	RH	$-R\times10^4$
8250	5.03	6.10	9065	4.26	4.70
9360	5.70	6.09	9750	4.55	4.67
10270	6.18	6.02	10270	4.83	4.70
0	$w = 9.47\times10^{-4}\,\Omega$ $\frac{w}{w_0} = 1.015$		0	$w = 7.71\times10^{-4}\,\Omega$ $\frac{w}{w_0} = 0.825$	

Alloy IV contained 69.4 atomic percent of *Ag*. The plate was 0.083 mm. thick.

TABLE XVIII.

HALL effect for $(Au\text{-}Ag)_{IV}$

H	$T = 287^\circ$ K.		$T = 90^\circ$ K.		$T = 20^\circ.3$ K.		$T = 14^\circ.5$ K.	
	RH	$-R\times10^4$	RH	$-R\times10^4$	RH	$-R\times10^4$	RH	$-R\times10^4$
9220	5.55	6.02	4.77	5.17	4.12	4.47	4.08	4.43
9760	5.76	5.90	5.12	5.25	4.40	4.51	4.26	4.37
10270	6.20	6.04	5.41	5.27	4.66	4.54	4.55	4.43
0	$w=9.8\times10^{-4}\Omega$ $\frac{w}{w_0} = 1.01$		$w=8.43\times10^{-4}\Omega$ $\frac{w}{w_0} = 0.875$		$w=7.92\times10^{-4}\Omega$ $\frac{w}{w_0} = 0.82$		$w=7.90\times10^{-4}\Omega$ $\frac{w}{w_0} = 0.82$	

Alloy V contained 90.9 atomic percent of *Ag*. The plate was 0.082 mm. thick.

TABLE XIX.

Hall effect for $(Au\text{-}Ag)_V$

H	$T = 290°$ K.		$T = 90°$ K.		$T = 20.°3$ K.		$T = 14.°5$ K.	
	RH	$-R\times10^4$	RH	$-R\times10^4$	RH	$-R\times10^4$	RH	$-R\times10^4$
9065	6.62	7.31	5.88	6.49	5.22	5.76	5.16	5.69
9760	7.23	7.42	6.30	6.45	5.59	5.73	5.66	5.80
10270	7.52	7.32	6.58	6.40	5.98	5.82	5.86	5.71
0	$w=5.29\times10^{-4}\Omega$ $\frac{w}{w_0}=1.025$		$w=3.81\times10^{-4}\Omega$ $\frac{w}{w_0}=0.735$		$w=3.40\times10^{-4}\Omega$ $\frac{w}{w_0}=0.66$		$w=3.40\times10^{-4}\Omega$ $\frac{w}{w_0}=0.66$	

Alloy VI contained 97.8 atomic percent of *Ag*. The plate was 0.093 mm. thick.

TABLE XX.

Hall effect for $(Au\text{-}Ag)_{VI}$

H	$T = 290°$ K.		$T = 90°$ K.		$T = 20.°3$ K.		$T = 14.°5$ K.	
	RH	$-R\times10^4$	RH	$-R\times10^4$	RH	$-R\times10^4$	RH	$-R\times10^4$
9220	7.10	7.70	6.79	7.37	6.41	6.95	6.38	6.92
9500	—	—	—	—	—	—	6.59	6.94
9760	7.56	7.75	7.22	7.41	6.82	6.99	6.73	6.90
10270	7.95	7.74	7.71	7.51	7.13	6.94	7.09	6.90
0	$w=25.2\times10^{-5}\Omega$ $\frac{w}{w_0}=1.04$		$w=12.7\times10^{-5}\Omega$ $\frac{w}{w_0}=0.525$		$w=8.7\times10^{-5}\Omega$ $\frac{w}{w_0}=0.36$		$w=8.7\times10^{-5}\Omega$ $\frac{w}{w_0}=0.36$	

TABLE XXI.

Substance	Atomic percent. *Ag*	$R_{290°}$	$R_{90°}$	$R_{20°.3}$	$R_{14°.5}$	$\frac{R_{90°}}{R_{290°}}$	$\frac{R_{20°.3}}{R_{290°}}$	$\frac{w_{90°}}{w_0}$	$\frac{w_{20°.3}}{w_0}$	$[D_L]_{T=290°}$	$[D_L]_{T=90°}$	$[D_L]_{T=20°.3}$
Au	0	7.2×10^{-4}	7.6×10^{-4}	9.8×10^{-4}	9.8×10^{-4}	1.05	1.36	0.285	0.035	3.2×10^{-7}	12.6×10^{-7}	133×10^{-7}
$(Au\text{-}Ag)_I$	2.0	6.8	6.6	6.7	6.5	0.97	0.98	0.49	0.30	2.3	4.8	8.03
$(Au\text{-}Ag)_{II}$	10.7	5.6	5.25	3.7	3.7	0.82	0.66	0.69	0.585	1.05	1.12	1.23
$(Au\text{-}Ag)_{III}$	30.0	5.6	4.7	3.6	3.7	0.77	0.64	0.825	0.755	0.61	0.57	0.52
$(Au\text{-}Ag)_{IV}$	69.7	6.0	5.2	4.5	4.4	0.87	0.75	0.875	0.82	0.64	0.64	0.60
$(Au\text{-}Ag)_V$	90.9	7.35	6.45	5.75	5.75	0.88	0.79	0.735	0.66	1.45	1.79	1.80
$(Au\text{-}Ag)_{VI}$	97.8	7.7	7.4	6.95	6.9	0.96	0.91	0.525	0.36	3.2	6.1	8.5
Ag	100	8.0	8.2	10.15	9.9	1.02	1.27	0.23	0.0091	4.95	23.1	720

In Table XXI are collected my results for alloys of gold and silver. In it are given results for the HALL coefficient R_T, and its temperature coefficient $\frac{R_T}{R_{290}}$, for the LEDUC constant $D_L = \frac{R}{w}$, and for the temperature coefficient of the restistance without a magnetic field. All are expressed in c. g. s. units.

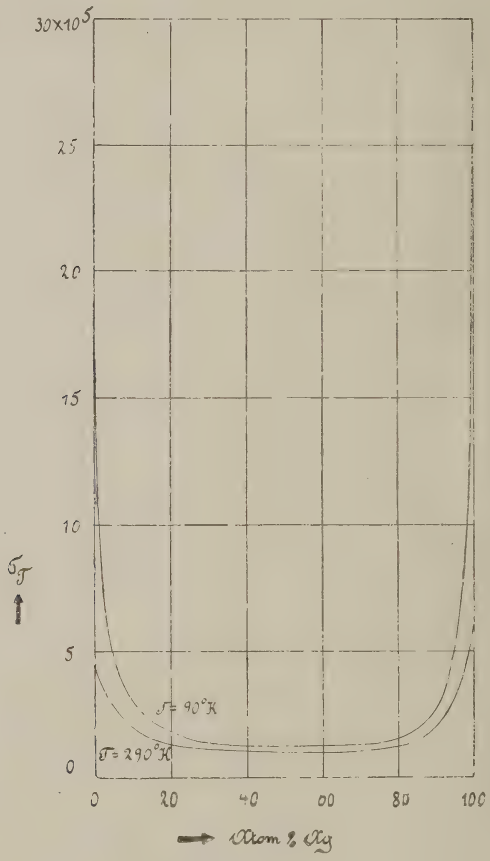

Fig. 1.

Fig. 1 is a diagram of the electrical conductivity (σ) at $T = 290°$ K. and at $T = 90°$ K. as a function of the atomic percentage of Ag. The unit in which the conductivity is expressed is the reciprocal of the resistance in ohms of a 1 cm. edged cube. The conductivity was calculated from the analyses. (See a previous paper [1])).

At lower temperatures the characteristic curves become steeper. This is strongly marked at hydrogen temperatures as is shown by the measurements of Kamerlingh Onnes and Clay [2]) on a gold-silver alloy containing about 0.4 % *Ag*, and by Clay's [3]) measurements on *Au-Ag* alloys with various compositions. The latter measurements have been confirmed by mine, and have been further extended to embrace cases of average and of small content of *Au*. For these cases, somewhat similar results were obtained as with small content of *Ag*: the addition of a small quantity of gold to pure silver causes such an enormous decrease in the conductivity that, for instance, an admixture of 2 atomic per cent of gold reduces the conductivity (expressed in the above measure) from 71.10×10^6 to 1.35×10^6. The curves expressing the temperature quotient $\frac{\sigma_T}{\sigma_0} = \frac{w_0}{w_T}$ as a function of the atomic percentage follow a similar course. The researches of Kamerlingh Onnes and Clay [4]) on various gold wires have shown that the degree of purity of a metal can be very accurately gauged from a determination of the temperature coefficient of its resistance at hydrogen temperatures.

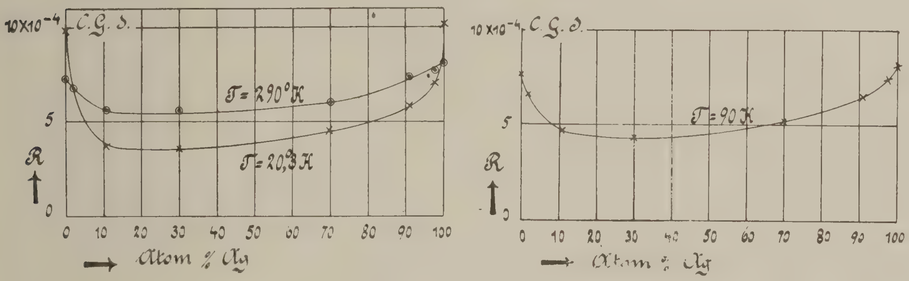

Fig. 2 en 3.

Figs. 2 and 3 show the Hall coefficient R_T at temperatures of 290° K., 90° K. and 20°.3 K. as a function of the atomic percentage of *Ag*. The curves resemble those which give the electrical conductivity and the temperature quotient of the resistance as functions of the atomic percentage. (Cf. KAMERLINGH ONNES and BENGT BECKMAN, Comm. N⁰. 130*c*). When silver is gradually added to pure gold, the HALL coefficient at low temperatures diminishes, at first rapidly, and then more slowly, until, with a mixture of about equal quantities of *Au* and *Ag*, a large change in the composition occasions only a very small change in the HALL effect. The lower the temperature the steeper is the descent of the curve. For instance, when a 2 % admixture of silver is added to pure gold the HALL coefficient diminishes

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[1]) Bengt Beckman. Upsala Univ. Årsskrift 1911.

[2]) H. Kamerlingh Onnes and J. Clay. Comm. N°. 99, 1907.

[3]) J. Clay. Comm. N°. 107*d*, 1908.

[4]) See note 2.

at $T = 20°.3$ K. from 9.8×10^{-4} to 6.7×10^{-4},
at $T = 90°$ K. from 7.6×10^{-4} to 6.6×10^{-4},
at $T = 290°$ K. from 7.2×10^{-4} to 6.8×10^{-4}.

Hence a small *Ag* impurity in gold occasions only a small variation of the HALL effect at $T = 290°$ K. which, however, becomes more appreciable at lower temperatures. On the other hand, as is evident from the measurements of A. VON ETTINGSHAUSEN and W. NERNST [1]), E VAN AUBEL [2]) and A. W. SMITH [3]), the addition of a small quantity of *Sn* or *Sb* to *Bi*, which exhibits an unusually large HALL effect, occasions even at ordinary room temperature a great change in the HALL effect.

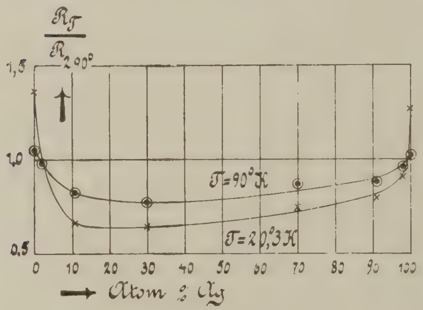

Fig. 4.

In Fig. 4 are shown the curves of the temperature quotients $\frac{R_{90°}}{R_{290°}}$ and $\frac{R_{20 \cdot 3°}}{R_{290°}}$ as functions of the atomic percentage of *Ag*. These curves have the same general features as those of Figs. 1, 2 and 3.

In Fig. 5 is shown the relation between *R* and *T* for some *Au*-*Ag* alloys. The course of the curves between 20° K. and 90° K. is not quite certain, as no observations could be made between hydrogen and oxygen temperatures. These portions of the curves are therefore indicated by dotted lines. With *Ag* and

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[1]) A. VON ETTINGSHAUSEN and W. NERNST: Wied. Ann. **33**, p. 474, 1888.
[2]) E. VAN AUBEL: C. R. **135**, p. 786, 1902.
[3]) A. W. SMITH: Phys. Rev. **32**, p. 178, 1911.

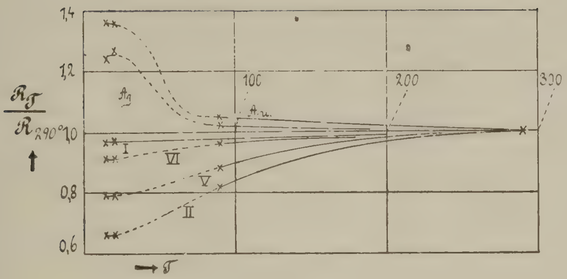

Fig. 5.

Au the HALL coefficient increases as the temperature falls. This increase takes place chiefly in the temperature region $20° < T < 77°$ K. In the hydrogen region, $20°.3 > T > 14°.5$, R is constant within the limits of accuracy. A very small diminution of the HALL coefficient is exhibited by the alloy $(Au\text{-}Ag)_I$ with 2 % Ag at low temperatures. At low temperatures alloys with more than 2 % of Ag show a distinct diminution in the HALL effect, which is greatest for alloys of medium concentrations. Thus alloy III with 30 % Ag gives $\frac{R_{20°}}{R_{290°}} = 0.64$. With Au and Ag the ratio $\frac{R_{90°}}{R_{290°}}$ differs but very little from 1, while with alloys of medium concentration it differs considerably from 1. Of the alloys with a large percentage of Au, a distinct diminution of the HALL effect at low temperatures is already exhibited by alloy VI, with 2 % of Au.

In fig. 6 is shown the relation between the LEDUC constant $D_L = \frac{R}{w}$ and the atomic percentage of Ag at $T = 290°$ K. and $T = 90°$ K. This constant is the tangent of the angle of rotation of the equipotential lines in unit field. The curves are of the same nature as the conductivity-silver percentage diagrams; at lower temperatures they become steeper. When two per cent of Au is dissolved in Ag D_L at $T = 20°.3$ K. sinks from 720×10^{-7} to 8.5×10^{-7}. It is worth noting that with alloys of medium concentration D_L is approximately constant throughout the whole temperature region $290° > T > 14°.5$; this holds for $10.7 \leqq x \leqq 90.9$ that is to say, for alloys in which the percentage of neither component is less than 10.

With alloys which may be regarded as dilute solutions, hence

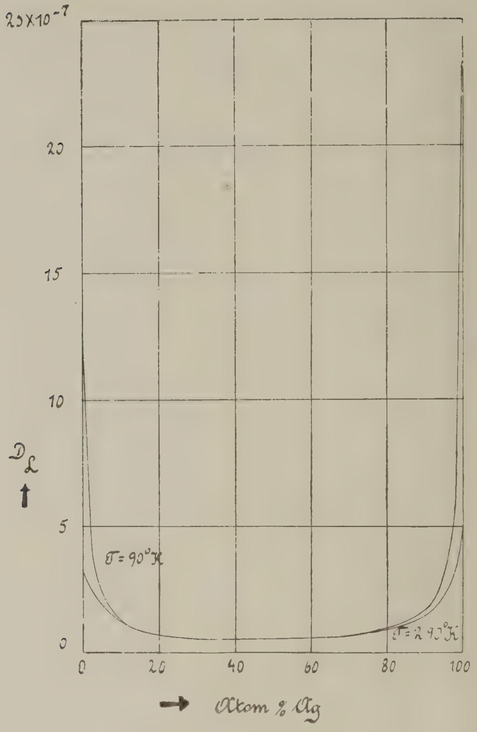

Fig. 6.

for $0 \leqq x \leqq 11$ and $90 \leqq x \leqq 100$, as a rule R is, to a first approximation, a linear function of the temperature quotient $\frac{w_T}{w_0}$ ($T = 290°$ K., 90° K., 20°.3 K.). Only the alloys with a large percentage of Ag at $T = 20°.3$ K are an exception to this rule.

At $T = 290°$ K. the HALL coefficient for dilute solutions is proportional to the conductivity $\sigma_{290°}$.

It would undoubtedly be of the greatest importance to systematically extend these investigations of the HALL effect in alloys at low temperatures, which I have, to my regret been obliged to confine to a single series of alloys, and to further investigate alloys of different types. I hope to continue this research as soon as I can find a suitable opportunity.

I gratefully acknowledge my indebtedness to Prof. KAMERLINGH ONNES who invited me to undertake these investigations of the HALL effect at low temperatures.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 132^{d}.

H. KAMERLINGH ONNES and **BENGT BECKMAN**.
On the HALL effect, and on the change in electral resistance in a magnetic field at low temperatures. VIII. The HALL-effect in Tellurium and Bismuth at low temperatures down to the melting point of hydrogen.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **28 December 1912**, p. 1044—1051).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and BENGT BECKMAN. *On the* HALL-*effect, and on the change in electrical resistance in a magnetic field at low temperatures.* VIII. *The* HALL *effect in Tellurium and Bismuth at low temperatures down to the melting point of hydrogen.*

§ 20 [1]. *The* HALL *effect in Tellurium.* The measurements were made with a short period WIEDEMANN galvanometer. The primary current was $I = 0.2$ amp. Two plates were investigated, both constructed from the purest MERCK tellurium. The first plate Te_{pI} was compressed in a steel mould, and the second plate Te_{pII} was cast in a steel mould. The first plate was very brittle. Both plates were circular with a diameter of 1 cm. The electrodes were platinum wires $^1/_2$ mm. in diameter, and were fused into the plates. To these platinum wires the leads were then soldered. The specific resistance and its temperature coefficient were different for the two plates; at $T = 289°$ K. w_{sp} was twice as great for the first as for the second. The resistance temperature coefficient for Te_{pI} was always negative over the whole temperature region $289° > T > 20°.3$ K. Te_{pII} on the other hand exhibited a minimum in the resistance below $T = 70°$ K.

The thickness of the plate Te_{pI} was 1.175 mm; its resistance

at $T = 290°$ K. was $w = 0.8\ \Omega$
20° 3 $w = 3.0$
and again at 290° $w = 1.0$;

at low temperatures therefore the resistance is considerably increased; cooling, moreover, caused an increase in the resistance at ordinary temperature, which is probably due to the production of small fissures.

At $T = 290°$ the specific resistance was 1.95×10^8 c. g. s. We obtained the following results (RH and R given in c. g. s. units):

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[1] The sections of this Communication are numbered as continuations of Comm. No. 132*a*.

TABLE XXV.

HALL effect for $Te_{p\,I}$

H in gauss	$T = 290°$ K.		$T = 20°.3$ K.	
	RH	R	RH	R
3750	14.65×10^4	39.1	16.1×10^4	43.1
5640	22.4	39.7	—	—
7260	29.0	40.6	31.9	44.2
9065	35.4	39.1	41.4	44.5
10270	40.2	39.1	46.6	45.3

At $T = 290°$ the specific resistance of $Te_{p\,II}$ was 1.01×10^8 c. g. s. The plate was 1.88 mm. thick. The change in the resistance with temperature is shown in Table XXVI and in fig. 5 [1]).

TABLE XXVI.

Variation of the resistance of Tellurium, $Te_{p\,II}$, with temperature.

T	w
289° K.	0.212Ω
170.8	0.146
162.3	0.144
153.1	0.141
141.8	0 136
90	0.119
80	0.117
69.5	0.113
20 3	0.122
17.7	0.124
14.5	0.126

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[1]) The diagrams are numbered as continuations of those in Comm. No. 132*a*.

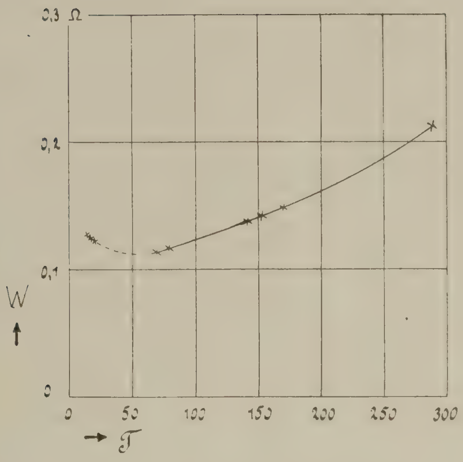

Fig. 5.

Hence, as has already been mentioned, the resistance of the plate $Te_{p\mathrm{II}}$ attains a minimum at about 40° to 60° K. This behaviour is somewhat similar to that found by DEWAR to be characteristic of bismuth containing only a slight amount of impurity, and by J. KOENIGSBERGER, O. REICHENHEIM, K. SCHILLING [1]) for a kind of pyrites, for magnetite, metallic titanium and metallic zirconium, a phenomenon explained by J. KOENIGSBERGER by the dissociation of electrons from the atoms.

With this plate, too, an increase of the resistance was observed on returning to ordinary temperature $T = 290°$ K. after having cooled it to hydrogen temperatures. In this case, however, it was much smaller than with $Te_{p\mathrm{I}}$, and was, at the most, 5 $^0/_0$. We obtained the results given in Table XXVII (following page).

At any definite temperature R is practically constant for various fields; at lower temperatures there is an indication that R diminishes somewhat in the stronger fields; this is most marked at hydrogen temperatures at which R_0 (R for $H = 0$) is about 5 $^0/_0$ greater than R for $H = 10000$.

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[1]) J. KOENIGSBERGER: Jahrb. d. Rad. u. Elektr. **4**, p. 158, 1907. O. REICHENHEIM: Inaug.-Diss. Freiburg i. Br. 1906. J. KOENIGSBERGER and K. SCHILLING: Ann. d. Phys. **32**, p. 179, 1910.

TABLE XXVII.

Hall effect for $Te_{p\,II}$

H in gauss	$T = 291°$ K.		$T = 89°$ K.		$T = 20°.3$ K.		$T = 14°.5$ K.	
	RH	R	RH	R	RH	R	RH	R
3720	6.90×10^5	185.5	7.85×10^5	210.5	7.98×10^5	214.5	7.85×10^5	211
5680	10.55	186	11.95	210	12.1	213	11.85	208.5
7260	13.6	187	—	—	15.4	212	15.0	206.5
9065	16.75	185	18.75	207	19.05	210	18.65	205.5
10270	18.85	183.5	21.25	207	21.4	208.5	21.0	204.5

For both plates the Hall effect increases at lower temperatures, while the ratio $\dfrac{R_{20°\ \text{K.}}}{R_{290°\ \text{K.}}}$ is the same. This is very remarkable, for the plates are completely different with regard to their specific resistance, resistance temperature coefficient and absolute magnitude of the Hall effect. For both plates the value of the Hall effect is small compared with that obtained by A. v. Ettingshausen and W. Nernst [1]), 530, and also by H. Zahn [2]), and the electrical conductivity is also small. According to the researches of A. Matthiessen and M. von Bose [3]), F. Exner [4]), W. Haken [5]), J. F. Kröner [6]) and others, various modifications of tellurium occur; according to Kröner it exhibits dynamical allotropy. The two modifications have very different conductivities. The specific gravity of the plate $Te_{p\,II}$ was 6.138; this is perhaps connected with the circumstance that it cooled slowly after casting, and that it was subjected to local heating when fusing in the electrodes. For a preparation very quickly cooled Kröner gives a specific gravity

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[1]) A. von Ettingshausen and W. Nernst. Sitz. Ber. Akad. d. Wiss. Wien. **94**, p. 560, 1886.

[2]) H. Zahn. Ann. d. Phys. **23**, p. 146, 1907.

[3]) A. Matthiessen and M. von Bose. Pogg. Ann. **115**, 385, 1862.

[4]) F. Exner. Sitz. Ber. Akad. d. Wiss. Wien. **73**, 285, 1876.

[5]) W. Haken. Inaug. Diss. Berlin 1910.

[6]) J. F. Kröner. Inaug. Diss. Utrecht 1912.

6.28, while some of his specimens had a specific gravity as low as 5.8. The modification with the lowest specific gravity seems to have the smallest electrical conductivity.

§ 21. *The* HALL *effect in Bismuth crystals.* In Table XIII, Comm. N°. 129*a*, we gave results of measurements of the HALL effect in bismuth crystals for the case in which the crystalline axis is perpendicular to the field, and the main current runs in the direction of the axis. To these we are now in a position to add results for the case in which the field is parallel, and the main current perpendicular, to the axis. For these measurements we used one of the crystal prisms which had been used by VAN EVERDINGEN (Suppl. No. 2) in his measurements, choosing the most regular of the three (2, 3 and 5 l. c.) which had been found suitable for this purpose (cf. p. 82 l. c.).

In the following Table are given R, H and RH in c. g. s.

At ordinary temperature and in weak fields RH is negative, as was first discovered by VAN EVERDINGEN and subsequently confirmed by J. BECQUEREL [1]).

In stronger fields RH becomes positive, as was also found to be the case by VAN EVERDINGEN and BECQUEREL. We may, however, incidentally remark that the initial negative values found by BECQUEREL are much greater than ours, and that with him zero is reached in much stronger fields than with us. This leads us to suspect that the initial negative values we have obtained are to be ascribed to some cause which occasioned their occurrence to a much higher degree in BECQUEREL's experiments; this would be the case, for instance, if our bismuth were purer than his, but still not yet quite free from impurity. If that were the case, then with absolutely pure bismuth we should, perhaps, at ordinary temperature, obtain nothing but increase of RH with the field, the rate of increase being slower in the initial stages.

But one can still quite well imagine, however, that at higher temperatures negative values can be obtained in weaker fields in the course of the change which RH as a function of H undergoes with the temperature. The part played by admixture would then be restricted to a displacement of the temperature at which

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[1]) J. BECQUEREL, C. R. 154, p. 1795. June 24, 1912.

TABLE XXVIII.

Hall effect for a Bismuth crystal with its axis parallel to the field.

$T = 290°$ K.			$T = 90°$ K.			$T = 20°.3$ K.			$T = 14°.5$ K.		
H	*RH*	*R*	*H*	*RH*	*R*	*H*	*RH*	*R*	*H*	*RH*	*R*
1000	$-\ 0.05 \times 10^3$	$-\ 0.05$	1005	$+\ 3.4 \times 10^3$	$+\ 3.4$	1670	$+\ 5.2 \times 10^3$	$+\ 3.11$	2970	$+\ 8.55 \times 10^3$	$+\ 2.88$
1660	+ 0.09	+ 0.06	2490	7.8	3.13	2740	7.95	2.90	5680	15.5	2.73
2970	+ 0.86	+ 0.29	4220	12.2	2.89	3720	10.45	2.81	8260	22.1	2.69
3720	+ 1.57	+ 0.42	5710	15.9	2.78	5680	15.4	2.71	10270	27.4	2.67
5680	+ 4.12	+ 0.72	7300	20.0	2.75	7260	19.3	2.66			
7260	+ 6.60	+ 0.91	9110	24.7	2.71	9065	24.0	2.65			
9065	+ 9.8	+ 1.08	10320	27.7	2.69	10270	27.2	2.65			
10270	+11.9	+ 1.19									

a negative value could still just appear, and this temperature would be higher for bismuth of greater purity than for impure bismuth. This would be analogous to the diminution of the negative effect at lower temperatures in the case discussed in § 14 of Comm. No. 129*c* in which the axis stands perpendicular to the field.

At lower temperatures we found the HALL effect positive in all fields, which is not what BECQUEREL found to be still the case at liquid air temperatures. It is further worth noting that RH shows no further change with temperature below the temperature of liquid air. This makes it important to amplify the measurements given in Table XIII for the axis perpendicular to the field by others at the temperature of liquid air.

It is seen from Fig. 6 that for fields greater than 2000 gauss at low temperature, and in fields greater than 6000 gauss at ordinary temperature, RH is clearly a strictly linear function of the field. If we write

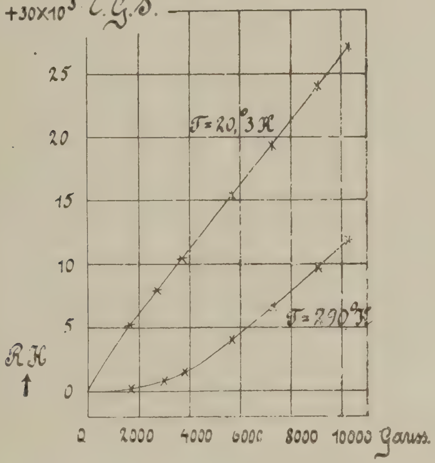

Fig. 6.

$$RH = a' H + b'$$

in this region, we obtain

$$\begin{array}{lll} T = 290^\circ \text{ K.} & T = 90^\circ \text{ K.} & T = 20^\circ.3 \text{ K.} \\ a' = +1.7 & a' = +2.56 & a' = +2.56 \\ b' = -5600 & b' = +1300 & b' = +1100 \end{array}$$

§ 22. *Remark upon the increase in the resistance of bismuth in a magnetic field.* A friendly remark by Prof. H. DU BOIS leads us to a further development of our ideas concerning the occurrence of a maximum in the isopedals for the increase in the resistance of bismuth.

Our measurements make it probable that the maximum found by Blake at the temperature of liquid air must be ascribed to the presence of impurity or to some modification occasioned, for instance, by mechanical treatment, and that this maximum is not obtained with pure normal bismuth at these temperatures. The values which we obtained at the boiling point of hydrogen make it also certain that neither is a maximum to be found between the temperatures of liquid air and of liquid hydrogen. In the region of hydrogen temperatures a falling off in the rate of increase of the resistance of the bismuth wires is clearly apparent. The existence of this diminution has been proved twice, and on each occasion for different currents (and, as is evident from the table, for various fields). But a maximum, that is to say, a return to smaller values, we have not obtained. From the course of the curves given by Bengt Beckman in Comm. No. 130*a*, it still remains possible that the phenomenon reaches a limiting value. From various analogous phenomena we might quite well expect something of this kind to happen at extremely low temperatures. In Comm. No. 129*a* we commented under I, § 2, upon the uncertainty as to whether a maximum is reached at these temperatures, or rather an asymptotic approach would be found to be made to a limiting value, stating that „Perhaps as the purity increases the maximum in the isopedals is displaced towards lower temperatures." The measurements we have made with the plates *Bi* lay further emphasis upon the „perhaps." As the temperature falls to 20° K. the plates Bi_{pI}, Bi_{pII}, which were not so pure as the wire, exhibit no diminution in the rate of increase. And yet, on account of the greater impurity suspected in these plates, they should be expected to exhibit a maximum between 14° 5 and 73°K., if there were a maximum for pure bismuth at temperatures lower than 14°.5 K. and if this maximum were displaced towards lower temperatures only by an increase in the purity of the material. In contrast with this we here find that only the diminution in the rate of increase remains between 20° K. and 14°.5 K. Further experiments upon different bismuth preparations are of course highly desirable.

COMMUNICATIONS

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BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 132e.

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H. KAMERLINGH ONNES and E. OOSTERHUIS. Magnetic Researches. VII. On paramagnetism at low temperatures *(Continued)*.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **25 Januari 1913**, p. 1166—1172).

EDUARD IJDO. — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and **E. OOSTERHUIS.** *Magnetic Researches.* VII. *On paramagnetism at low temperatures (continued).*

§ 9. *Crystallized manganese sulphate.* The salt was procured from MERCK as puriss. pro analysi. The results were [1]:

TABLE VII.

Crystallized manganese sulphate $Mn\,SO_4 \,.\, 4\, H_2O$. (I)

T	$\chi \,.\, 10^6$	$\chi \,.\, T \,.\, 10^6$	Limits of H.	Bath
288°.7 K.	66.3	19140	10000—17000	Air.
169 .6	111.5	18910	8000—17000	Liquid ethylene.
77 .4	247	19120	6000—16000	Liquid nitrogen.
70 .5	270	19030		
64 .9	292	18950		
20 .1	914	18370	4000—16000	Liquid hydrogen.
17 .8	1021	18170		
14 .4	1233	17760		

Down to and at nitrogen temperatures, this substance follows pretty much the law of CURIE.

§ 10. *Anhydrous manganese sulphate.* All the water was driven out of the salt by heating.

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[1] Prof. WEISS has kindly informed us that in the determination of standards of susceptibility in Zürich, for this substance $\chi = 66.77 \,.\, 10^{-6}$ at 14°.2 C. was found.

The results are given in Table VIII.

With anhydrous manganese sulphate another divergence from the law of CURIE over the whole field of low temperatures was found. Down to nitrogen temperatures, however, it is only a disturbance of the first kind. At hydrogen temperatures a further disturbance shows itself which is not unlike the disturbances with solid oxygen, and at any rate belongs to a kind of disturbances that we have not yet been able to reduce to a definite type. It is remarkable that just as with crystallized ferrous sulphate the presence of molecules of water of crystallization causes a diminution of the quantity Δ' to a very small value in comparison with that of the anhydrous substance, here too Δ' becomes less by the adding of molecules of water of crystallization, and to such a degree, that, if one does not go below nitrogen temperatures, Δ' appears to have become $= 0$, whereas with anhydrous salt $\Delta' = 24°$.

TABLE VIII.

Anhydrous manganese sulphate. $Mn\,SO_4$ (I). $\Delta' = 24°$.

T	$\chi \cdot 10^6$	$\chi (T + \Delta').10^6$	Limits of H.	Bath.
293°.9K.	87.8	27910	6—17 Kilog.	Air.
169 6	144.2	27920	5—17 „	Liquid ethylene.
77 .4	274.8	27870	5—16 „	Liquid nitrogen.
64 .9	314.5	27960		
20 .1	603	26590	4—16 „	Liquid hydrogen.
17 .8	627	26210		
14 .4	636	24420		

If we calculate the number of magnetons for the crystallized salt with $C = \chi\, T$ ($\Delta' = 0$) and for the anhydrous with $C' = \chi\, (T + \Delta')$ and with $\Delta' = 24°$, we find the same number of magnetons in both cases, viz. 29. This is one less than is found in the solution [1]).

§ 11. *Further observations upon ferrous sulphate and ferric sulphate.* After the conclusion of the investigation treated in Comm. N⁰. 129*b*, we turned to the determination of the water contained in the preparations ferrous sulphate I and ferrous sulphate III.

Prof. VAN ITALLIE kindly investigated the preparations and found that they contained ferric as well as ferrous sulphate. They cannot therefore be taken as a reliable basis for calculations of the number of magnetons, and to make these possible the measurements will be repeated with purer preparations.

The quantitative result arrived at in Comm. N⁰. 129*b* concerning the appearance of disturbances of the first kind in CURIE's law and the possibility of finding the constant of CURIE for these substances by means of a correction, still retains its value.

As regards the ferric sulphate, which the measurements in § 4 of Comm. N⁰. 129*b* referred to, the admixture of water may be put at about $^1/_7$ in first approximation. The molecular susceptibility of ferrous sulphate is therefore $^1/_7$ smaller than that of ferric sulphate, so that valency shows its influence in this iron salt also; all this in contradiction to what was observed in § 4.

We must also remark, that the sign and the order of magnitude of the corrections which would be necessary to deduce the number of magnetons for the pure materials from the measurements of the ferrous sulphate I of our Comm. N⁰. 129*b* and those of the crystallized ferrous sulphate of KAMERLINGH ONNES and PERRIER in Comm. N⁰. 122*a*, make it seem possible that there is a double analogy between ferrous sulphate and manganese sulphate. Just as in manganese sulphate the number of magnetons in the crystallized and in the anhydrous substance is equal, the same would be found for crystallized and anhydrous ferrous sulphate (viz. 26) (if for the anhydrous substance CURIE's constant is calculated with the help of the correction by $\Delta' = 31°$), and in further analogy with manganese sulphate, this number with ferrous sulphate is also one less than in the solution, if for the latter one may take the number, that has been found by Wills[1]).

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[1]) P. WEISS. Journal de physique, 1911, p. 976.

Should the disappearance of Δ' with the introduction of water molecules be ascribable to the increase of distance between the iron atoms which is caused thereby, then it would be possible that with different contents of water of crystallization Δ' decreases with the increase of the number of molecules of water of crystallization. We intend therefore to examine a salt in this respect that crystallizes[2]) with a series of different numbers of molecules of water of crystallization, and from that to deduce a possible dependence of Δ' upon the density.

§ 12. *Platinum.* A small cylinder of pure platinum from Heraeus was examined. The susceptibility changes very little with the temperature. On account of its small value it is difficult to determine χ accurately. The results are contained in Table IX.

TABLE IX.

Platinum I.

T	$\chi \cdot 10^6$	Limit value of H in Kilogauss.
290°.2 K.	0.973	11—17
77 .4	1.061	
20 .1	1.080	
14 .4	1.087	

The value at ordinary temperature lies about the middle of those of Owen, 0.80 resp. 0.89, Honda 1.097, Koenigsberger 1.35, Finke 1.06 (all at 18° C.). If one wished to go so far with the application of the rule $C' = \chi (T + \Delta')$ that one applied it to platinum also, then it would follow from this that $\Delta' = 2440°$, and for the number of magnetons n calculated from C' the value $n = 10$.

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[1]) P. Weiss. Journ. de physique. 1911. p. 977.

[2]) Compare the investigation of Mlle Feytis, C. R. 153, p. 668, 1911 on the influence of the successive molecules of water of crystallization upon χ. This might be the consequence of a change in Δ' with an unchanged number of magnetons.

§ 13. *Dysprosium Oxide.* Referring to the data of § 7, we observe that, as will also appear from a further communication of KAMERLINGH ONNES and PERRIER, all the values of χ which occur there must be increased in the ratio of 1 : 1.065. By applying this correction also the difference from the value at ordinary temperature found by Mlle FEYTIS which we remarked upon in § 2 of Comm. N⁰. 122*a* and which was due to an error of calculation, is reduced to a divergence within the limits of accuracy; hence the dysprosium oxide appears to have been about in the same condition as the sample used by her. Our conclusions undergo no change by the correction.

§ 14. *Oxygen.* The susceptibility of liquid oxygen has been determined by KAMERLINGH ONNES and PERRIER by two methods. It has now also been investigated by the attraction method in about the same way as the susceptibility of liquid hydrogen in Comm. N⁰. 122*a*. An evacuated cylindrical glass tube was hung in the magnetic field and then the repulsion measured that the tube underwent when the surrounding space was filled with liquid oxygen. The value found at $T = 90°.1$ K. agrees well with that in Comm. N⁰. 116; the small difference at the other temperatures is explained by the fact that the temperatures could not be very accurately ascertained.

In the following table the values found stand beside those of KAMERLINGH ONNES and PERRIER according to their formula $\chi \sqrt{T} = 2.284.10^{-3}$.

The question naturally arises whether the behaviour of liquid oxygen can also be represented by the formula $C' = \chi (T + \Delta')$. If we assume that $\Delta' = 71°$ this comes out pretty well, as appears from Table XI in which the values of χ are taken from KAMERLINGH ONNES and PERRIER Comm. N⁰. 116, Table III.

TABLE X.

Liquid oxygen.

T	$\chi \cdot 10^6$ K. O. and O.	$\chi \cdot 10^6$ (K. O. and P.)
90°.1 K.	241.1	240.6
79.1	258.1	256.8
70.2	270.7	272.6

When the atoms are assumed to be free in the molecule C' gives for the number of magnetons 11 per atom (calculated 11.04), and on the hypothesis that in the liquid two gas molecules are rigidly connected it gives 11 per molecule of two atoms.

TABLE XI.

Representation of the susceptibility of liquid oxygen by the formula $\chi(T+\Delta')=C', \Delta'=71°$.

T	$\chi \cdot 10^6$	$\chi(T+71) \cdot 10^6$
90°.1	240.6	38760
71.35	269.6	38420
64.9	284.2	38620

From $\chi\ (T+\Delta')=38600$ (the mean of the numbers in the table) with $\Delta'=71°$ one finds for $T=293°$ K.

$$\chi_{293° \text{K.}} = 106.0 \times 10^{-6}.$$

This is very close to the value for gaseous oxygen at 20° C. found by WEISS and PICCARD [1]), from which follows 7 magnetons for each of the oxygen atoms assumed to be rigidly connected.

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[1]) P. WEISS et A. PICCARD. C. R. 155, p. 1234, 1912.

Seeing that above 20° C. gaseous oxygen follows CURIE's law [1]), it seems to be by some chance that our formula with $\Delta' = 71°$ gives that figure.

The graphic representation of $^1/_\chi$ as a function of T, if our formula actually remained true up to 20° C., would consist of two intersecting lines that have their point of intersection just at the temperature at which the value quoted is determined, which certainly would be a curious coincidence.

Another possibility which Prof. WEISS suggests in a kind private communication, is that there might be discontinuity in the region between 0° C. and — 183° C. which has not been investigated, by which it remains accidental that the continuation of the line for liquid oxygen cuts that for gaseous oxygen just at 20° C. There is much to be said for this explanation. It is quite possible that the change of density between liquid oxygen and gaseous oxygen makes Δ' into 0. This would be in accordance with what was deduced in § 10 for the influence of the water molecules upon the value of Δ' for manganese sulphate, and moreover quite in accordance with WEISS's idea that the molecular field essentially depends upon the density.

We can further observe, that the change of density, which takes place discontinuously with evaporation, can take place continuously by an indirect transition. In the above line of thought, if we assume that the divergence for liquid oxygen from CURIE's law may be defined by a Δ' and pay attention to the change of the number of magnetons which must be assumed in that case, the graph which represents $^1/_\chi$ for oxygen of a given density as a function of the temperature would be as in magnetite a succession of straight lines perhaps connected by rounded off pieces. The magnetic equation of state which expresses the susceptibility as a function of density and temperature (with a view to determining which the experiments of KAMERLINGH ONNES and PERRIER were undertaken, see Comm. N^0. 116 § 1) would be given by a series of similar lines, differing for the different densities.

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[1]) Prof. WEISS who has particularly investigated this question, kindly tells us that the experimental results of CURIE agree so well with CURIE's law within the limits of observation errors that Δ' could not be more than + 8° or — 8°.

We must not forget that it is by no means established that in the case of oxygen the divergence from CURIE's law is determined by a Δ' which changes with the density, and that it obviously may be due to an association of molecules into complexes with a diminution of the number of magnetons.

However this may be, our attention is again drawn to the important question whether the divergences from CURIE's law depend upon a peculiarity of the atom within the single molecule or from the approach of the molecules up to a very small distance.

In § 3 of Comm. N°. 122*a* by KAMERLINGH ONNES and PERRIER, it is said that preliminary experiments with mixtures of liquid oxygen and nitrogen, which will soon be replaced by better final ones and which were suggested by the above mentioned association hypothesis, seemed to indicate that bringing the molecules to a greater distance by dilution in the liquid state has no influence of importance upon the divergences from CURIE's law. We would put the question here in this form: whether Δ' is a quantity which as peculiar to the atom in the single molecule can also be found in the gaseous state or whether it can only be developed by bringing the molecules into immediate vicinity of each other. Further experiments with oxygen ¹) already planned must decide this.

(To be continued).

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¹) As this communication is going to press, these experiments have advanced so far, that we may accept with great probability as the result of them, that gaseous oxygen of 90 times the normal density obeys CURIE's law down to — 130° C.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 132^f.

⁂

H. KAMERLINGH ONNES and **Mrs. ANNA BECKMAN**.
On piezo-electric and pyro-electric properties of quartz at low temperatures down to that of liquid hydrogen.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **22 Februari 1913**, p. 1277—1281).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and Mrs. ANNA BECKMAN. *On piezo-electric and pyro-electric properties of quartz at low temperatures, down to that of liquid hydrogen.*

§ 1. *Introduction.* As many qualities of solid bodies are much simplified at very low temperatures by the considerable decrease of the caloric motion, it seemed desirable to examine also the piezo- and pyro-electric effects under these probably favourable circumstances. In order to make a preliminary inquiry into this branch of the subject we have measured the piezo-electric modulus of quartz, perpendicular on the axis, down to the temperatures of liquid hydrogen.

Then we have also, at the temperatures of liquid air and liquid hydrogen, observed the pyro-electric phenomenon of quartz, which FRIEDEL, CURIE and others have examined at higher temperatures.

§ 2. *Measurements of the piezo-electricity of quartz at low temperatures.* The measurements were effected by the generation of electricity on a quartz plate, which was kept at low temperatures and compared with a similar plate at ordinary temperature. The generated charge was measured with a quadrant electrometer. Both the plates were of the same sort as is used in the ordinary CURIE's instrument, that is to say, they were cut out of the crystal parallel to the optical axis and with the broadest side perpendicular to one of the electrical axis.

They were 7—8 cm. long, 2 cm. broad and 0.06 cm. thick. The two broad sides were coated with tin 1). One of the tin coatings of each plate was earthed, the two others were metallically connected with one another and with one pair of quadrants of the

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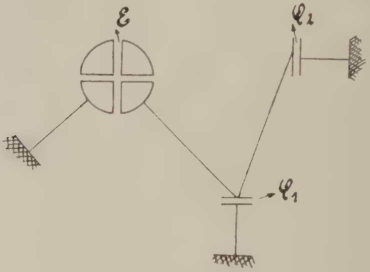
1) The tinfoils were apt to get loose from the plate in the liquid oxygen, which gave rise to blisters; it would of course be better to employ a platinized quartz plate, silvered: Then, too, the use of cementing material between the metal coating and the quartz would be obviated.

electrometer, as is shown in the figure. The other pair of quadrants was earthed.

All the connections were enclosed in brass tubes, which were in connection with the earth. The electrometer needle was kept at a constant potential of 120 volts.

The quartz plate Q_1 was suspended in an earthed metal case and carried a scale pan, on which weights could be placed, in order to stretch the plate; Q_2 was put in a DEWAR glass; its



lower end was fastened in a brass support, which was carried by the cap of the vacuum vessel; the uppermost end was suspended by a brass rod to one arm of a balance, whose other arm carried a scale, which could be loaded with weights. In order to be able to close the vessel hermetically (which was quite necessary), and at the same time make the free movement of the rod through the cover possible, it was simplest, for these preliminary measurements, to use an elastic india rubber tube which closed round the rod and the tube in the cap. As we shall see this had only a slight effect on the relative measurements.

Within the glass, the quartz plate and the support were surrounded by a brass net in connection with the earth.

The measurements were made in the following way: first the plate Q_1 was stretched by a weight (500 gr.) and the deviation of the electrometer needle was observed. Then this plate was earthed, and when the connection with the earth was broken, the weight was removed and the deviation of the electrometer to the other side was observed. The sum of these deviations is proportional to the quantity of electricity generated. Then the electricity which was generated on Q_2 was measured in the same way. Immediately before and after the measurements the electrometer was calibrated with a Weston element. The sensibility changed very little.

The insulation was generally very good, so that there was seldom any need of making corrections for leakage.

Always five or seven turnings of the electrometer needle were observed. From these the eventual corrections for incomplete insulation could be calculated.

§ 3 *Results.* I. Both the quartz plates at room temperature ($T = 290°$ K.).

The deflections were:

						mean values
Q_1	126.7	127.2	127.0	127.6	127.4	127.2
Q_2	163.7	164.0	163.6	163.2	163.3	163.6

The Weston element (1.018 volts) gave 34.4.

The capacity of the electrometer, of the connections to Q_1 and of Q_1 itself was about 150 cm.; that of the connection to Q_2 and of Q_2 was about 100 cm. By the cooling of Q_2 its capacity changes

II. Q_2 in oxygen boiling under a pressure of 21 cm. $T = 78°.5$ K.

			mean values
Q_1	130.6	130.1	130.3
Q_2	165.2	165.7	165.4

One Weston element 34.4.

III. Q_2 in boiling hydrogen. $T = 20°.3$ K.

				mean values
Q_1	129.6	130.5	130.0	130.0
Q_2	165.4	165.5	165.4	165.4

One Weston 34.4.

IV. Q_2 at ordinary temperature, $T = 290°$ K.

						mean values
Q_1	127.1	127.4	127.1	126.8	127.0	127.0
Q_2	162.5	163.0	162.8	163.1	162.7	162.8

One Weston 34.3.

In order to examine the influence of the elastic connection between Q_2 and the cap of the vacuum vessel, two measurements were made without the elastic tube, one at ordinary temperature and the other in liquid air. These gave

V. Q_2 at ordinary temperature, $T = 290°$ K.

						mean values
Q_1	126.2	126.8	127.7	127.5	127.1	127.0
Q_2	167.4	168.1	168.1	167.8	168.3	167.9

One Weston 34.3.

VI. Q_2 at the temperature of liquid air, $T = 80°$ K.

						mean values
Q_1	129.3	129.6	129.8	129.7	129.9	129.7
Q_2	168.8	169.3	170.1	169.2	169.4	169.4

One Weston 34.3

By immersing Q_2 into the bath of low temperature the deviations are thereby changed for both the plates. The change was at the measurement

II	$T = 78°.5$ K	$Q_1 + 2.4\,^0/_0$	$Q_2 + 1.1\,^0/_0$
III	20°.3	$2.2\,^0/_0$	$1.0\,^0/_0$
VI	80°.0	$2.1\,^0/_0$	$0.9\,^0/_0$

The electricity generated on Q_2 was thus at all events less than at ordinary temperature. The decrease was $1.3\,^0/_0$, $1.2\,^0/_0$, $1.2\,^0/_0$.

The influence of the elastic connection falls within the limits of errors of observation. In the absolute measurements the connection causes a decrease of about $3\,^0/_0$.

Thus we may conclude that the cooling from 290° K to 80° K causes a decrease of $1.2\,^0/_0$ in the piezo-electric modulus. A further cooling from 80° to 20° causes a much smaller change, it appears even less than $2\,^0/_{00}$. The importance of this result is perhaps that the change in the piezo-electricity by cooling to low temperatures seems to take place chiefly above the temperature of liquid air.

§ 4. *Pyro-electricity of quartz.* As has already been said, we also made some observations on the pyro-electricity of quartz at the temperature of liquid air and hydrogen. The pressure under which the liquid round Q_2 boiled was changed. By the change of temperature, which is the consequence thereof, a pyro-electric charge is generated on Q_2. The deflections of the electrometer were

for 90° K.	to 86°.5 K.	+27.5 mm.	or per degree:	+8.5 mm.	mean value per degree: 7.8 mm.
86.5	„ 82.5	+27.0	„ „ „ „	+6.5 „	
82.5	„ 78.5	+27.5	„ „ „ „	+8.5 „	
78.5	„ 90	—89.0	„ „ „ „	—7.5 „	
20°.3 K.	„ 15°.2 K.	+ 6.5	„ „ „ „	+1.4 mm.	1.6 mm.
15.2	„ 20.3	— 7.8	„ „ „ „	—1.6 „	
between 20°.3 and 15°.8		± 14.3	(double deflection)	± 1.7 „	

The deviation 7.8 per degree at the temperatures of liquid oxygen
1.6 per degree at the temperatures of liquid hydrogen
has by an increase of temperature the same direction as by a stretching of the plate.

We note that the generated pyro-electric charge is about proportional to the absolute temperature.

We wish to record our heartiest thanks to Mr. G. HOLST, assistent at the physical laboratory, for his assistance at our experiments.

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 132g.

◆

BENGT BECKMAN. Measurements on resistance of pyrite at low temperatures, down to the melting point of hydrogen.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akademie van Wetenschappen te Amsterdam*, **22 Februari 1913**, p. 1281—1284).

EDUARD IJDO — PRINTER — LEIDEN.

BENGT BECKMAN. *Measurements on resistance of a pyrite at low temperatures, down to the melting point of hydrogen.*

In an earlier publication [1]) I examined resistance as a function of temperature in the case of a pyrite crystal from Gellivare, Malmberget, Sweden. Those measurements embraced the temperature interval + 100° C. to — 193° C. The resistance was well represented by the formula

$$W = W_0 \, e^{at} , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where W_0 is the resistance at 0° C and t the temperature on the centrigrade scale. The spec. resistance at 0° C in ohms per cube of 1 cm was $w_0 = 0.00294$; a was 3.53×10^{-3}.

The measurements were made with a WHEATSTONE's bridge. The ends of the crystal were galvanized with copper; as electrodes amalgamated copper plates were used. The resistance at 0° C was 0.101 ohms. To determine the magnitude and the variation of the contact resistances and of the connections with the temperature, a little copper prism of the same dimensions as the crystal was placed between the electrodes and short-circuited, and the resistance of the short-circuited crystal support and the connections were measured at the various temperatures.

I have now had the opportunity of continuing these measurements on a pyrite through a larger temperature-interval (down to — 258° C). This last investigation was made in the cryogenic laboratory of the University of Leiden, and for the opportunity I owe the director of the laboratory, Prof. H. KAMERLINGH ONNES, great thanks.

To obtain these measurements I have used another method, which eliminates the possible errors of the contact resistances. The crystal was pressed between two copper electrodes, through which the current was conveyed to it. Two other electrodes were firmly pressed against the longest side of the crystal. The voltage between these was measured with the compensation apparatus [1]).

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[1]) BENGT BECKMAN. Uppsala Univ. Årsskrift 1911. Mat. o. naturvetenskap 1, p. 28.

In Table I the results of the measurements in Upsala 1910 are given and in Table II these last results of 1912. The values $\left(\frac{W}{W_0}\right)_{\text{calc}}$ are calculated from the formula (1), where now

$$a = 3.59 \times 10^{-3}.$$

The results are well represented by this formula. The values of $\frac{W}{W_0}$ at low temperatures that were found in the last observations are in better agreement with the formula than the earlier ones.

The results for $t = -78°.6$ C and $-193°$ C in these deviate a little

TABLE I.

Change of the resistance of pyrite with the temperature. Measurements in Upsala, 1911.

t	$\left[\frac{W}{W_0}\right]_{\text{obs.}}$	$\left[\frac{W}{W_0}\right]_{\text{calc.}}$
+ 100°.9 C.	1.422	1.436
+ 54°.2	1.223	1.215
+ 44°.5	1.180	1.173
0°	1	1
— 78°.6	0.726	0.754
— 193°	0.508	0.495

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[1]) See H. Diesselhorst. Zeitschrift f. Instrumentenkunde **26**, p. 182, 1906, where Fig. 2 gives a survey of the mounting.

TABLE II.

Change of the resistance of pyrite with the temperature. Measurements in Leiden, 1912.

t	$\left[\frac{W}{W_0}\right]_{obs.}$	$\left[\frac{W}{W_0}\right]_{calc.}$
+ 15°.8 C.	1.063	1.058
— 183°	0.519	0.520
— 252°.8	0.405	0.404
— 258°	0.390	0.396

from the calculated values, but in different directions. The deviations do not exceed 4°/₀, which corresponds to a difference of 0.004 ohms at the most.

The last measurements may also serve to control whether the results of the earlier ones were not fully accurate owing to the contact resistances. The deviations that I have just mentioned might arise from this source of error, but, as they go in different directions at $t = -78°.6$ C and $t = -193°$ C, one is inclined to think that these deviations may originate in other errors too, for instance in variations of the temperature bath at $t = -78°.6$ C. (solid carbonic acid and ether).

O. Reichenheim ¹) and J. Koenigsberger ²) have examined pyrite from Val Giuf, Graubünden and have found a minimum of resistance at about $t = -10°$ C. This pyrite has a specific resistance of 0.0240 at 0° C, thus eight times larger than mine. An explanation of this difference of the conductivity is given by J. Koenigsberger ³).

My pyrite shows no minimum of resistance above — 258° C. The resistance throughout the whole temperature-interval follows the formula (1), which is the same, mathematically, as

$$\frac{1}{W}\frac{dW}{dt} = \text{constant}.$$

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¹) O. Reichenheim. Inaug. Dissert. Freiburg 1906.

²) J. Koenigsberger: Jarhbuch der Rad. u. Elektr. **4**, p. 169, 1907.

³) J. Koenigsberger. Phys. Zeitschr. **13**, p. 282, 1912.

It seems very probable that there does not exist any minimum below -258° C, but that the resistance at still lower temperatures approaches asymptotically to a limit value, as is the case in, for instance, not perfectly pure gold and platinum.

A. WESELY[1] has recently examined a pyrite crystal from the same place of origin, Malmberget, Gellivare. He found a still smaller specific resistance, $w_0 = 0.00247$ and a temperature coefficient at 0° C of 0.00228.

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[1] A. WESELY. Phys. Zeitschr. **14**, p. 78, 1913.

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COMMUNICATIONS

FROM THE

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UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory

N°. 132.

H. KAMERLINGH ONNES and BENGT BECKMAN. On the Hall effect, and on the change in resistance in a magnetic field at low temperatures. VI. The Hall effect for nickel, and the magnetic change in the resistance of nickel, mercury and iron at low temperatures down to the melting point of hydrogen.

—— and **BENGT BECKMAN**. On the change induced by pressure in electrical resistance at low temperatures. I. Lead.

BENGT BECKMAN. On the Hall effect etc. VII. The Hall effect for gold-silver alloys at temperatures down to the melting point of hydrogen.

H. KAMERLINGH ONNES and **BENGT BECKMAN**. On the Hall effect etc VIII. The Hall effect in Tellurium and Bismuth at low temperatures, down to the melting point of hydrogen.

—— and **E. OOSTERHUIS**. Magnetic Researches. VII. On paramagnetism at low temperatures *(Continued)*.

—— and **Mrs. ANNA BECKMAN**. On piezo-electric and pyroelectric properties of quartz at low temperatures down to that of liquid hydrogen.

BENGT BECKMAN. Measurements on resistance of pyrite at low temperatures, down to the melting point of hydrogen.

(*Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **30 November 1912**, p. 881—893, **28 December 1912**, p. 1035—1051, **25 Januari 1913**, p. 1166—1172, **22 Februari 1913**, p. 1277—1281).

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